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Development of a simulated natural carbonation test and durability of selected CEM II concretes

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DEVELOPMENT OF A SIMULATED NATURAL CARBONATION TEST AND DURABILITY OF SELECTED CEM II CONCRETES

By

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A Thesis presented in application for the Degree of Doctor of Philosophy

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DECLARATION

I hereby declare that I am the author of this thesis, and that the work of which this thesis is a record has been composed by me, that all references cited have been consulted, and that it has not been previously presented for a higher degree.

Moray D Newlands

CERTIFICATE

This is to certify that **Moray D Newlands** has completed research under my supervision, and that he has fulfilled the conditions of Ordinance 14 of the University of Dundee, so that he is qualified to submit this thesis in application for the Degree of Doctor of Philosophy.

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ABSTRACT

The study reported here investigates the development of a simulated natural test for benchmarking the carbonation resistance of hardened concrete. The European Committee for Standardisation (CEN) had devised a draft simulated natural test and although initial Round Robin test results had shown poor repeatability, the test had potential for development as a reliable benchmarking tool.

The current study identified the areas of variability in the test as being (i) non-conformance to the test storage environmental conditions and (ii) variability in production of concrete specimens. A storage room with active control over temperature and relative humidity was proposed for the test. An in house CO_2 injection system was developed and environmental monitoring showed that temperature, relative humidity and atmospheric CO_2 concentration in the test chamber were all within the proposed CEN test limits. In addition, a two stage normalisation procedure was established to reduce variability in the production of concrete specimens. A repeatability test demonstrated that implementing environmental control and the normalisation procedure considerably reduced the variability of the test.

A selection of CEM I and CEM II concretes, containing condensed silica fume (10%, 15%, 20%) and metakaolin (10%, 15%, 20%), were benchmarked against a PC/PFA 30% Reference Mix to assess the effect of cement type on carbonation resistance. All concretes were tested on an equal strength basis of 37N/mm^2, the minimum grade requirement in BS EN 206-1, using the modified CEN test and a previously developed accelerated carbonation test. A reasonable correlation was found between the 20 weeks accelerated and 2 year CEN carbonation depths indicating that accelerated methods may be useful in testing relative carbonation performance. A detailed permeation and hydration study highlighted the importance of both the physical and chemical properties of concrete in resisting carbonation. A relationship between water/PC ratio and carbonation was established and a tentative water/PC upper limit of 0.65 proposed for 37N/mm^2 concrete.

Three additional coarse aggregate types, Thames Valley gravel, crushed limestone and crushed granite were also tested and were shown to have a minimal effect on the carbonation resistance of concrete. The influence of fines (particles <125µm, including cement) on carbonation resistance was also studied. Adjusting the fine/coarse aggregate ratio to increase the fines content was found to be detrimental to the particle packing characteristics of the concrete. Fractional replacement of the fine aggregate with limestone filler was found to increase the packing density of the concretes, reduce the near surface permeation properties and improve carbonation resistance. A tentative optimum fines content of 390-400kg/m^3 was proposed.

A multi-regressive model which considered the near surface physical and chemical properties was developed to estimate long term carbonation performance. Comparison with published long term data proved difficult as did establishing which natural exposure environment each of the CEN Exposure classes represented. A long term natural exposure site was established to replicate outdoors sheltered conditions. Comparison of the 1 year data with that from the CEN test determined that outdoor sheltered conditions were not exactly replicated by the CEN Exposure Classes however, depths of carbonation were generally between those found in Exposure Class 1 and Exposure Class 2 of the enhanced CEN test.

PUBLICATIONS

JONES, M R, DHIR, R K, NEWLANDS, M D, and ABBAS, A M O, 'A study of the CEN test method for measurement of the carbonation depth of hardened concrete', Materials and Structures, Vol 33, March 2000, pp135-142.

JONES, M R, NEWLANDS, M D, ABBAS, A M O, DHIR, R K, 'Comparison of 2 Year Carbonation Depths of Common Cement Concretes Using the Modified Draft CEN Test', Materials and Structures, (In Press)

JONES, M R, DHIR, R K, NEWLANDS, M D, ABBAS, A M O, 'Benchmarking the carbonation of hardened concrete', Concrete Durability and Repair Technology, Proceedings of Creating With Concrete, Ed R K Dhir and M J McCarthy, University of Dundee, 1999, pp299-309

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The concrete construction industry has an unmistakable contribution to make to our quality of life. Within the UK alone, the construction industry as a whole, including associated materials companies and professional services, accounts for some 10% of the Gross Domestic Product and provides employment for around 1.5 million people (DETR, 2000). In May 1999, the Department of the Environment, Transport and the Regions published a new strategy for Sustainable Development in the United Kingdom, with the aim of simultaneously achieving social, economic and environmental objectives and one major area of concern was the implementation of sustainable construction practices (DETR, 1999).

The relentless and necessary drive towards creating a global sustainable environment has led to the increasing use of waste materials as a component in concrete construction. Industrial by-products, such as pulverised-fuel ash (PFA) from coal-fired power generators and condensed silica fume (CSF) from ferro-silicon alloy manufacturing, can enhance concrete properties. The inclusion of waste materials also means that, in some cases, the Portland cement (PC) content of concrete may be reduced potentially leading to lower embedded energy levels and reduced material costs (Hendricks and Jensen, 1999). The perceived benefits from the use of industrial by-products led to the development of a new European cement standard, BS EN 197-1:2000. Table 1.1 details the twenty seven cement types now permitted for use in BS EN 197-1. Approximately ten of these are currently used in the UK however this number is constantly increasing as engineers become aware of the economic benefits of new materials.

In 1998, it was estimated that approximately £20bn of the £45bn annual turnover in the UK construction industry was spent on repair and maintenance of existing structures (DETR, 1998). Given the prevalence of reinforced concrete used in structures, durability of the material is a concern in achieving economic goals. Durability provisions in traditional concrete standards have adopted an implicit stance. Specifying limits on bulk engineering properties, such as water/cement ratio, compressive strength, and cement content, have led to a prescriptive approach in design standards (BS 8110 and BS 5382). However, an explicit examination of the deterioration processes has shifted the prescriptive approach towards the development of performance based specifications for concrete construction.

Table 1.1 Cement types available for use as structural concrete according to BS EN 197-1.

Cement Type	BS EN 197-1 Cement Notation	Clinker Content, %	Content of other main constituents, %
Portland Cement	CEM I	95-100	-
Portland-Slag Cement	CEM II/A-S	80-94	6-20
	CEM II/B-S	65-79	21-35
Portland-Silica Fume Cement	CEM II/A-D	90-94	6-10
Portland Pozzolana Cement	CEM II/A-P	80-94	6-20
	CEM II/B-P	65-79	21-35
	CEM II/A-Q	80-94	6-20
	CEM II/B-Q	65-79	21-35
Portland-Fly Ash Cement	CEM II/A-V	80-94	6-20
	CEM II/B-V	65-79	21-35
	CEM II/A-W	80-94	6-20
	CEM II/B-W	65-79	21-35
Portland-Burnt Shale Cement	CEM II/A-T	80-94	6-20
	CEM II/B-T	65-79	21-35
Portland-Limestone Cement	CEM II/A-L	80-94	6-20
	CEM II/A-LL	80-94	6-20
	CEM II/B-L	65-79	21-35
	CEM II/B-LL	65-79	21-35
Portland-Composite Cement	CEM II/A-M	80-94	6-20
	CEM II/B-M	65-79	21-35
Blastfurnace Cement	CEM III/A	35-64	36-65
	CEM III/B	20-34	66-80
	CEM III/C	5-19	81-95
Pozzolanic Cement	CEM IV/A	65-89	11-35
	CEM IV/B	45-64	36-55
Composite Cement	CEM/V/A	40-64	36-60
	CEM V/B	20-39	61-80

A fundamental understanding of the environment in which the concrete will exist, coupled with a knowledge of how the concrete performs under specific circumstances, means the engineer can specify concrete to the desired performance. This performance-based specification philosophy has been adopted by CEN, the European Committee for Standardisation, in the development of BS EN 206-1, the new European concrete specification standard. In the UK, BS EN 206-1 has a complimentary British Standard, BS 8500 which is currently in draft form. The traditional exposure conditions in BS 8110-1 and BS 5328 have been replaced with Exposure Classes which now relate directly to the form of deterioration to which the concrete may be subjected.

The absolute performance of concrete should be established by means of a reliable durability test which directly assesses the resistance of concrete to a deterioration process (Concrete Society, 1996). Such repeatable and reproducible standardised test methods are scarce in the field of concrete technology and before the true performance-based specification philosophy can be applied, test methods must be developed that relate to the output parameters of the durability design methodology in BS EN 206-1 and BS 8500.

The most serious phenomenon affecting durability of reinforced concrete structures is the corrosion of embedded steel induced by carbonation of the cover concrete (Parrott, 1987). The ingress of carbon dioxide (CO_2) from the surrounding environment can lead to the loss of passivation of the steel reinforcement and, in the presence of moisture and oxygen, corrosion can occur. Approximately two-thirds of all concrete is utilized in residential, industrial and commercial buildings which are primarily at risk from carbonation induced corrosion (Parrott, 1996).

The ingress of CO_2, and subsequent carbonation induced corrosion, can affect all structures where the moisture saturation level of the concrete is sufficient to support both CO_2 ingress and steel oxidation, either continuously or cyclically, with different seasonal environmental exposure conditions (Jones et al, 2000). Although carbonation-induced corrosion is rarely catastrophic (Concrete Society, 1996), it affects serviceability and can be aesthetically and economically significant for large-scale property owners (Jones et al, 2000).

Figures 1.1 and 1.2 illustrate the detrimental effects of carbonation induced corrosion on serviceability of a concrete beam soffit and reinforced concrete window frame.

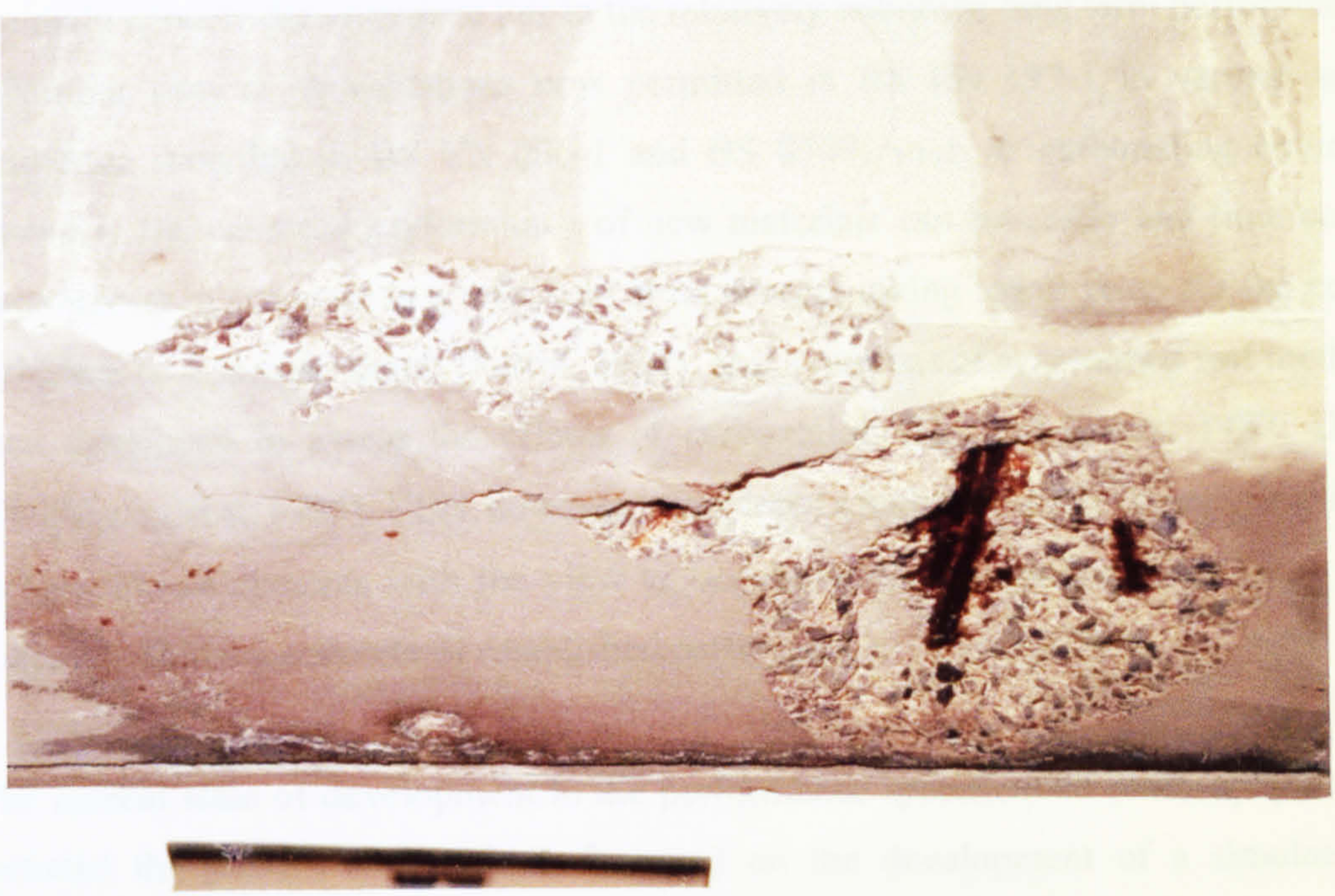


Figure 1.1 Carbonation-induced corrosion affecting serviceability of a beam. Corrosion has caused extensive spalling of the concrete exposing the steel reinforcement.

Figure 1.2 Carbonation-induced corrosion affecting aesthetics of a concrete window frame. Corrosion has caused spalling of the concrete exposing the steel reinforcement.

The main concern for engineers lies in the relatively unknown long term performance of the unfamiliar cement combinations now permitted in BS EN 197-1 in various aggressive conditions specified in BS EN 206-1 and BS 8500, such as carbonating environments. Assessing the potential performance of new materials can be costly and time consuming. Carbonation of concrete is a relatively slow process taking many years for the concrete to carbonate to a specific depth (Parrot, 1987), and a number of accelerated test methods have been developed to assess the effects of carbonation (Ho and Lewis, 1987; Dhir et al, 1989;Muller at al, 1995). CEN, however, considered a real-time test for comparing the relative carbonation of cements with the view to benchmarking the performance of an unknown concrete against a concrete of established performance (CEN, 1997).

The current state of development in the performance specification philosophy for concrete initiated the present study which focussed on the development of a simulated natural carbonation test method for determining the performance of concrete. The work undertaken applied the test methodology and multi regressive modelling, based on physical and chemical characteristics of concrete, to benchmark the long term carbonation performance of cement types currently unfamiliar to UK engineers.

1.2 SCOPE OF STUDY

The development of BS EN 206-1 and complimentary British Standard, BS 8500, led to the development of exposure classes based on deterioration mechanisms commonly associated with concrete. The current study aimed to develop a simulated natural carbonation test method which could be used to reliably benchmark concrete of unknown performance against a concrete of established performance. An examination of a draft 1 year test method by CEN was critically analysed and areas of potential development identified. A detailed monitoring programme of laboratory atmospheric conditions showed the need for active control over temperature, relative humidity and CO_2 concentration. The test method was substantially developed and repeatability determined.

The performance of cements less common in the UK, but having the potential for future use, were also considered. Materials such as condensed silica fume (CSF) and metakaolin(MK) were examined to determine the effects of the inclusion of these materials on the near surface properties of concrete in relation to carbonation resistance and performance pertaining to BS EN 206-1 and BS 8500.

Each concrete was physically and chemically characterised through a detailed hydration and permeation study and the influence of physical and chemical characteristics on carbonation resistance determined.

Given the physical nature of these fine particle cements, a theoretical examination of the effects of the unfamiliar cement types on the microstructure of concrete was undertaken. The effect of increasing the total fine particle content of the concrete was examined and the inclusion of a fine limestone filler was considered to improve the overall particle size distribution and packing density of the concrete constituent materials. The effect of using different coarse aggregate types commonly available in the UK was also considered to observe any effect on carbonation resistance.

The long term carbonation performance was estimated through formulation of a multi regressive model which took into account the near surface physical and chemical properties of the concrete. The long term results were compared to published data to determine whether the test methodology developed was replicating data obtained within the field. The long term benefits of improving the packing density of selected concretes was also examined to determine the potential trade off between concrete quality and carbonation resistance. A comprehensive climatological study of the UK and Europe was undertaken to ascertain variations in atmospheric conditions and how the simulated natural carbonation test may be used to replicate the natural environment.

A long term natural exposure was also established to compare data obtained from the simulated natural carbonation test and determine which Exposure Class in the simulated natural test represented exposure conditions in natural environment.

1.3 OBJECTIVES OF THE STUDY

The key objectives of the study are:

i) To develop a relatively quick, simulated natural carbonation test which can be reliably used to as a benchmarking tool and determine whether the test method can be used to reflect external micro and macro exposure conditions typically experienced in the UK and carbonation depths experienced in the field from published long term data.

ii) To scientifically appraise the carbonation performance of selected cements which are unknown to engineers in the UK but are currently permitted for use in BS EN 197-1. The physical and chemical influence of the selected cement types on carbonation resistance with regards to near surface properties are determined through a hydration and permeation study and the relative performance benchmarked against a concrete of established performance.

iii) To theoretically investigate the physical packing of concrete constituents containing fine particle cements and determine the influence of increasing the packing density of constituent materials on the physical and chemical properties of concrete and ultimately carbonation performance.

iv) To develop a multi-regressive model for estimating the long term carbonation performance of concrete, based on knowledge of the concrete physical and chemical characteristics and exposure conditions to which the concrete will be subjected. A long term environmentally monitored exposure site is established to provide a comparison between the simulated natural environment in the laboratory and external natural conditions.

1.4 OUTLINE OF THESIS

Chapter 2 is a review of current literature pertaining to the nature of concrete in structures and carbonation of concrete containing specific mix constituents. The review focusses on literature post 1987, as it was felt that, prior to this, Parrot had carried out a definitive review. The review considers existing work carried out on new materials which have come to the fore in the past 15 years. The Chapter also looks at the development of European Standards for cement and concrete specification.

Chapter 3 details the experimental programme, materials used throughout the project, concrete mix proportions and test methodologies.

The development of the simulated natural carbonation test is presented in Chapter 4. The pan European Round Robin undertaken by CEN is analysed, and proposed developments to the test methodology and equipment given. The results of an in-house repeatability study on the developed test are presented.

Chapter 5 details the development of the Reference Mix against which the concrete within the test programme will be benchmarked. Results of a 2 year study of CEM II concrete using the simulated natural carbonation test and previously developed accelerated carobonation tests are presented. The Chapter also examines the relationship between the Exposure Classes in the developed carbonation test and the relationship between simulated natural and accelerated carbonation testing.

Chapter 6 examines the role of total fines content on the carbonation resistance of concrete. CEM II concretes containing silica fume and metakaolin are examined, and the mixes analysed by means of a combined physical and chemical analysis tool. The effects of improving the packing density through the replacement of fractions of fine aggregate with a fine limestone filler are determined, with respect to permeation and hydration characteristics and subsequent carbonation performance.

Estimation of the long term carbonation performance of concrete is examined in Chapter 7. The 2 year carbonation data from the CEN Test is projected forward and compared with published long term carbonation data by means of a multi-regressive model. The long term benefits of the use of limestone filler in concrete is also examined with a view to potential trade-off between concrete quality and carbonation resistance. Details of the development of a long term outdoor exposure site are also given. The role of the hydration characteristics and permeation properties of the concrete are also examined to determine whether these characteristics can be used to assess the relative performance of concrete.

Chapter 8 gives overall conclusions arising from the study and details the practical implications of the work undertaken. Recommendations for further study are also given.

CHAPTER 2

REVIEW OF LITERATURE

2.1 INTRODUCTION

This chapter reviews the published literature pertaining to concrete durability, current standards specifying concrete for structural use and the detrimental effects of the process of carbonation on hardened concrete. In the main, the review focusses on the implications of using different cement types on carbonation resistance and assesses published long term data. A comparison of published carbonation data, normalised to 35 years using the established $d=kt^n$ equation is given. This has been supplemented by an appraisal of various models allowing prediction of long term carbonation performance.

2.2 VARIATION OF CONCRETE QUALITY

Concrete is a composite and complex material consisting of three main components; cement (including additions), water and aggregates. Four fundamental areas affecting concrete quality are now well established (CEB, 1992) and these are briefly described below:

i) Design: Form and complexity of section, detailing of section and reinforcement.
ii) Materials: Quality of cement/aggregates, cement, and reinforcement types.
iii) Execution: Quality of workmanship, batching, mixing, handling and placing.
iv) Curing: Length of curing, loss of moisture, loss of heat.

The variability of insitu concrete quality is quite different to that produced under standard laboratory conditions. The laboratory environment is very controlled with batching, mixing, production methods, and curing conditions standardised. However, it is difficult to control conditions on site due to a variety of reasons. For example, discrepancies in workmanship can be substantial and lead to a large reduction in structural integrity (Somerville, 1986) and depending on the type of member and quality of workmanship, insitu concrete strength can vary between 50-75% of a standard laboratory produced concrete at 28 days (Bungey and Millard, 1996) .

2.2.1 Near Surface Concrete Quality

Variation of concrete quality within a section is well established. Figure 2.1 shows a typical variation as described by Dewar (1982) and Kreijger (1990). It is widely accepted that the cover concrete is potentially the poorest quality concrete within a section and is therefore of major importance to the design engineer concerned with durability as this provides the first line of defence for any physical, chemical and mechanical attack on a concrete structure.

Kreijger (1990) proposed that the outer zones of concrete within a section can be divided into further layers or 'skins', Figure 2.1. The outermost layer, the 'cement skin', approximately 1 to 3μm thick, is composed of the finest aggregate particles and cement. This 'cement skin' also surrounds embedded steel reinforcement and coarse aggregate particles and contains the transition zone between mortar and aggregate or steel reinforcement. Beneath the cement skin lies a layered mortar structure, the 'mortar skin' (1 to 5mm thick), providing a stronger line of defence against the external environment and to the embedded steel. Beyond this lies the 'concrete skin' which contains the steel reinforcement and coarse aggregate.

2.3 PROCESS OF CARBONATION

2.3.1 Transportation Mechanisms in Concrete

The most common cause of durability problems in reinforced concrete structures is the corrosion of embedded steel (Parrott, 1987). In the majority of cases, the corrosion of steel reinforcing bars is expedited by the ingress of deleterious agents from the surrounding environment mainly in the form of ions, gases and moisture through pores and cracks (CEB, 1992). The ingress of such deleterious agents is normally through one or a combination of three primary transportation mechanisms: absorption, permeability and diffusion.

Although the three mechanisms work in different ways and are dependent on various factors, many deleterious agents often enter the cover concrete under a combination of the three. Figure 2.2 schematically illustrates the way in which the external environmental conditions and concrete microstructural properties are inter-related with the transportation mechanisms (CEB, 1992). The transportation mechanisms are also influenced by constituent material properties, in addition to the duration of moist curing and curing technique used.

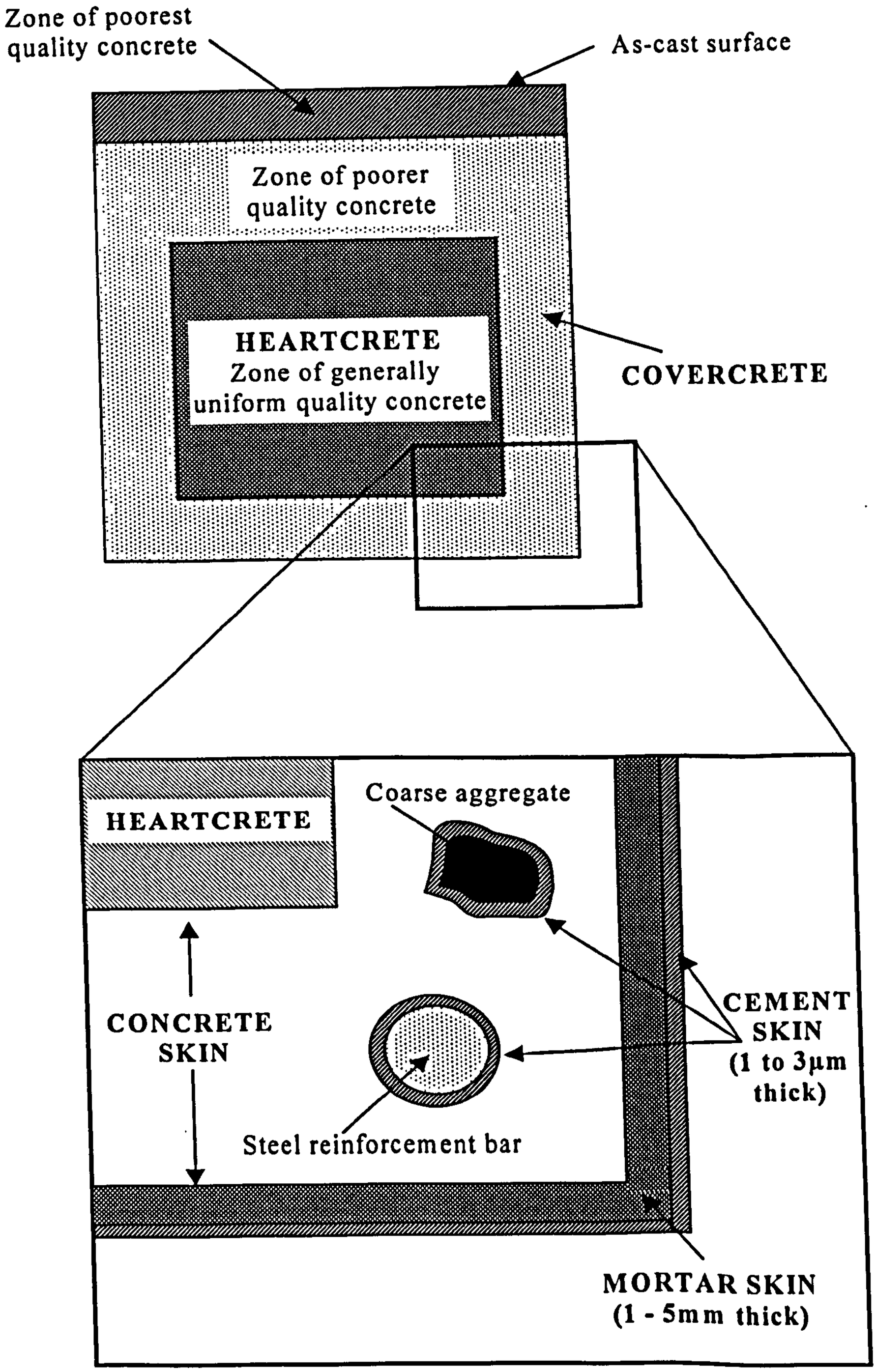


Figure 2.1 Variation in zones of quality in a typical concrete section, illustrating the concept of the 'skin effect' on the outer layers of concrete (After Dewar, 1982, and Kreijger, 1990).

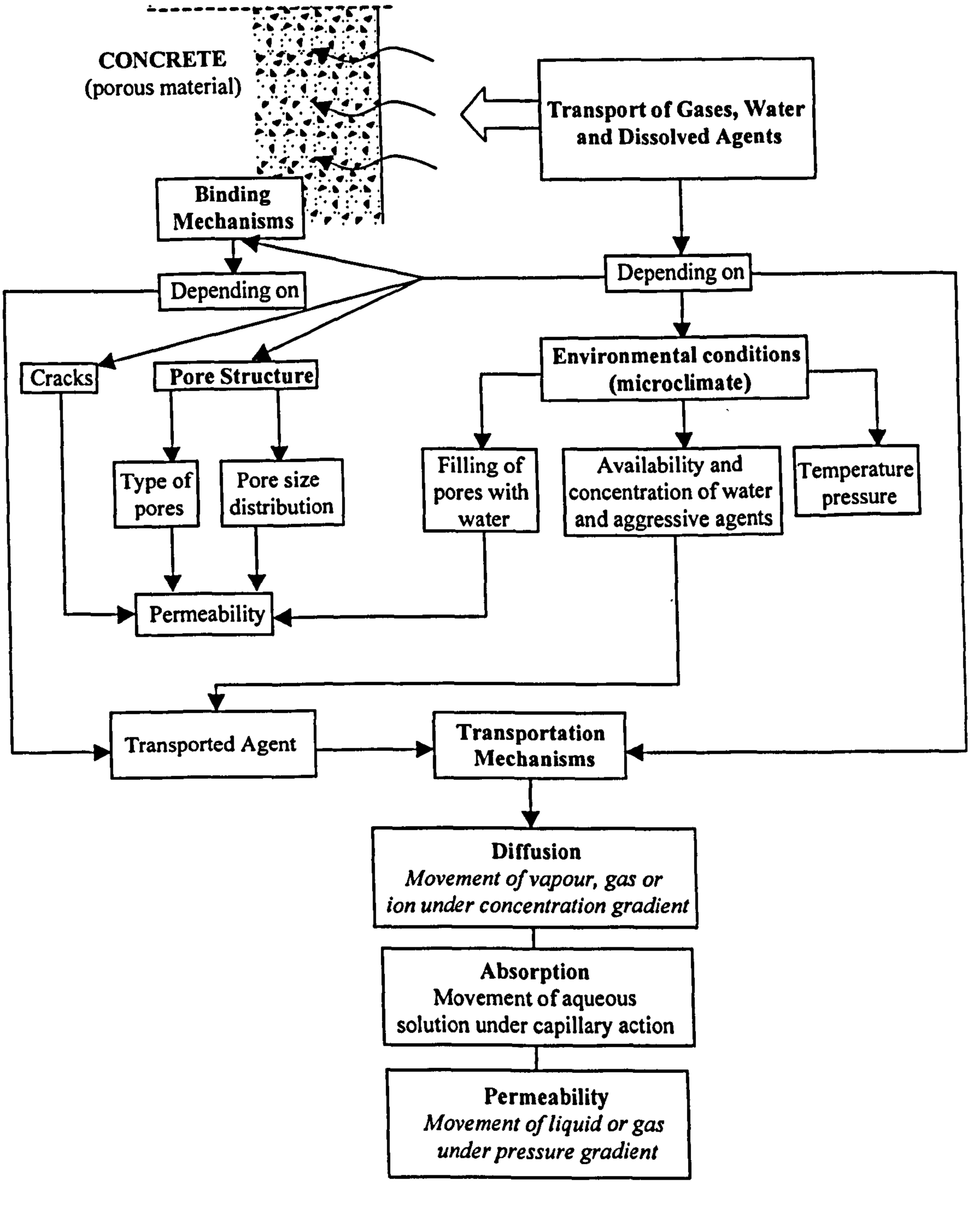


Figure 2.2 Interdependency between environmental effects, concrete microstructure, and transportation mechanisms on the ingress of aggressive media (CEB, 1992).

2.3.2 Physical Process

Carbon dioxide gas diffuses 10^4 times faster in air than in water (Parrott, 1987). However, lack of moisture will inhibit any chemical reaction. This indicates the significance of the exposure conditions in which the concrete is located. It has often been reported that a relative humidity ranging between 60 to 75 % is an optimum range favouring the progress of carbonation in concrete (Verbeck, 1958, Parrott 1987) as this allows the ingress of carbon dioxide whilst providing sufficient moisture for the chemical reaction to take place. Physically, the CO_2 molecule is 'linear' in shape with the carbon and oxygen atoms double bonded in a straight line (Ebbing and Wrighton, 1993). The molecule is very small and the prevention of ingress and movement through the concrete pores is somewhat limited by the pore size and tortuosity (Hewlett, 1998).

2.3.3 Chemical Process

Carbonation can be termed a diffusion-controlled chemical reaction, (Kropp, 1995). This means that the diffusion of the gas is the rate determining step of this chemical reaction. The chemical reaction proceeds sequentially, as the following chemical steps:

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (2.1)$$

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 \quad (2.2)$$

$$H_2CO_3 + CaCO_3 \leftrightarrow Ca(HCO_3)_2 \quad (2.3)$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O \quad (2.4)$$

CO_2 in its gaseous form, is not reactive and must dissolve in the moisture provided by the pore fluids to form carbonic acid, Equation 2.1. This reacts with the alkaline pore fluids and portlandite, to form carbonates, Equation 2.2. If the concentration of the CO_2 gas present is high enough, carbonic acid continues to form and react with the carbonates present to produce bicarbonates, Equation 2.3. This reaction continues as long as the bicarbonates can remain in solution and thus more CO_2 is required. The reverse reaction takes place when any of these are lost and calcium carbonate will then be precipitated until sufficient CO_2 gas has been released to stabilise the bicarbonate remaining in solution (Hewlett, 1998, Taylor, 1997).

The latter steps are likely to occur in exposures enriched with CO_2 gas, this being the case in accelerated CO_2 exposures performed in laboratory investigations where high CO_2 concentrations up to 100 % by volume of air may be used. Furthermore, the rapid reaction in

environments with a higher CO_2 concentration is due to the higher solubility of carbonic acid at higher concentrations (Hewlett, 1998).

2.4 ASSESSING THE QUALITY OF NEAR SURFACE CONCRETE

Traditional methods of specifying concrete have been based on the premise that given satisfactory bulk engineering properties, mainly the compressive strength, water/cement ratio, and cement content, the concrete will be of a durable nature (BSI, 1997). Although these bulk engineering properties are related to the quality of concrete, the relationships will only hold true for a given set of curing conditions and materials (Dhir et al, 1993). The array of cement types now available for use in UK and the rest of Europe means that concretes having similar bulk engineering properties, such as water/cement ratio and compressive strength, may well have a very a different physical and chemical make up. Therefore, it is vital that the quality of the surface and sub-surface layer of the concrete be assessed to ascertain whether the concrete, potentially, has adequate durability.

Most durability problems tend to occur over a long period of time and direct testing may not always be feasible. As most durability problems are, in part, a function of the ingress of aggressive media, concrete permeation properties can indicate potential durability. However, many permeation tests are sensitive to changes in concrete microstructure, age, curing and cement type. Table 2.1 summarises the main permeation tests used to assess the quality of surface and sub-surface quality of concrete.

2.5 CONCRETE DESIGN FOR DURABILITY

With approximately £20bn of the annual £45bn turnover within the UK construction industry spent on the repair and maintenance of existing structures, a deeper understanding of concrete durability is now of major importance (DETR, 1998). The Latham Report (1994) set an objective of a 30% reduction in construction costs within the UK and the realm of concrete durability has been identified as an area where major economic savings could be made.

2.5.1 Durability and Design Life

The term 'durability of a concrete structure' can have a number of meanings depending on the viewpoint of the individual, however the following generic definition may be applied:

Table 2.1 Common test methods used to determine near surface concrete permeation properties.

Test Method	Advantages	Disadvantages
Absorption Tests		
Initial Surface Absorption Test (ISAT) (BSI, 1996)	• Recognised standard method • In-situ / laboratory based	• Only measures surface quality
Covercrete Absorption Test (CAT) (Dhir et al, 1987)	• Measures cover depth quality • In-situ / laboratory based	• Only measures absorption • Partially destructive
Figg Water Permeability (Figg, 1973)	• Measures cover depth quality • In-situ / laboratory based	• Gives permeability "index" • Partially destructive
Water Absorption (Shallow immersion) (BSI, 1983)	• Quick, simple test • Direct measure of absorption (mass absorbed)	• Partially destructive (core samples) • Laboratory based
Water Absorption (Capillary rise)	• Simple • Direct measure of capillary rise (length of capillary saturation)	• Laboratory based
Permeability Tests		
Figg Air Permeability (Figg, 1973)	• Measures 40mm cover depth quality • In-situ / laboratory based	• Gives permeability "index" • Partially destructive
Intrinsic Air Permeability (Dhir et al, 1989a)	• Direct measure of concrete air permeability • Measure of cover depth quality	• Laboratory based (core samples)
CLAM (Montgomery and Adams, 1985)	• In-situ / laboratory based method	• Only measures surface quality
Diffusion Tests		
Oxygen Diffusivity (Grube and Lawrence, 1984)	• Direct measure of gas diffusion	• Laboratory based
Water Vapour Diffusion (Nilsson, 1980, Dhir et al, 1989c)	• Direct measure of vapour diffusivity • Can measure cover quality	• Laboratory based test • Sensitive to changes in concrete qaulity
Chloride Ion Diffusion (Dhir et al, 1990)	• Potential difference test a: quick	• Laboratory based • Concentration Difference test b: time consuming

'The ability of a concrete structure to maintain a specified level of technical performance to withstand the damaging effects of the environment and of its service conditions for a long period of time.' (Somerville, 1986)

Initially, design codes focussed on the structural aspects of concrete design assuming that, given adequate bulk engineering properties such as compressive strength, cement content, and water/cement ratio, concrete would withstand the actions of its service conditions and the effects of the surrounding environment (Harrison, 1995). This is the 'deemed to satisfy' approach.

However, it soon became clear with spiralling repair economics that a new approach to durability was required. Tuutti proposed that a concrete structure has a two stage 'Design Life', as shown in Figure 2.3 (Tuutti, 1982):

i) The initiation period (t_i) is governed by the ingress of the deleterious agent, in this case CO_2. During this period, the cover concrete carbonates and the carbonation front will eventually reach the steel reinforcement.

ii) The second stage is the propagation period (t_p) during which corrosion of the steel reinforcement commences provided there is sufficient availability of moisture and oxygen at the cathode and a high enough concentration of OH^- ion. The end of the design life is determined when the concrete structure reaches a predetermined criteria, such as spalling of the concrete cover due to reinforcement corrosion.

The significant factor in practice is the actual performance of a structure over a defined period and whether the level of this performance is satisfactory.

2.5.2 Corrosion of Embedded Steel

The main protection afforded by the concrete is through the formation of the passive γFe_2O_3 layer on the steel surface. Even in the presence of moisture and oxygen, which are essential for corrosion , if the γFe_2O_3 layer remains intact, corrosion will not occur (Schießl, 1984). It has also been argued that in addition to the passive oxide layer, a $Ca(OH)_2$ layer in contact with the steel also provides a degree of protection (Page and Treadaway, 1982). Using microscopy, the layer appeared to be a region consisting of an aggregate free zone of portlandite disrupted by inclusions of C-S-H gel (Leek, 1991). The ingress of CO_2 reacts with the alkaline pore

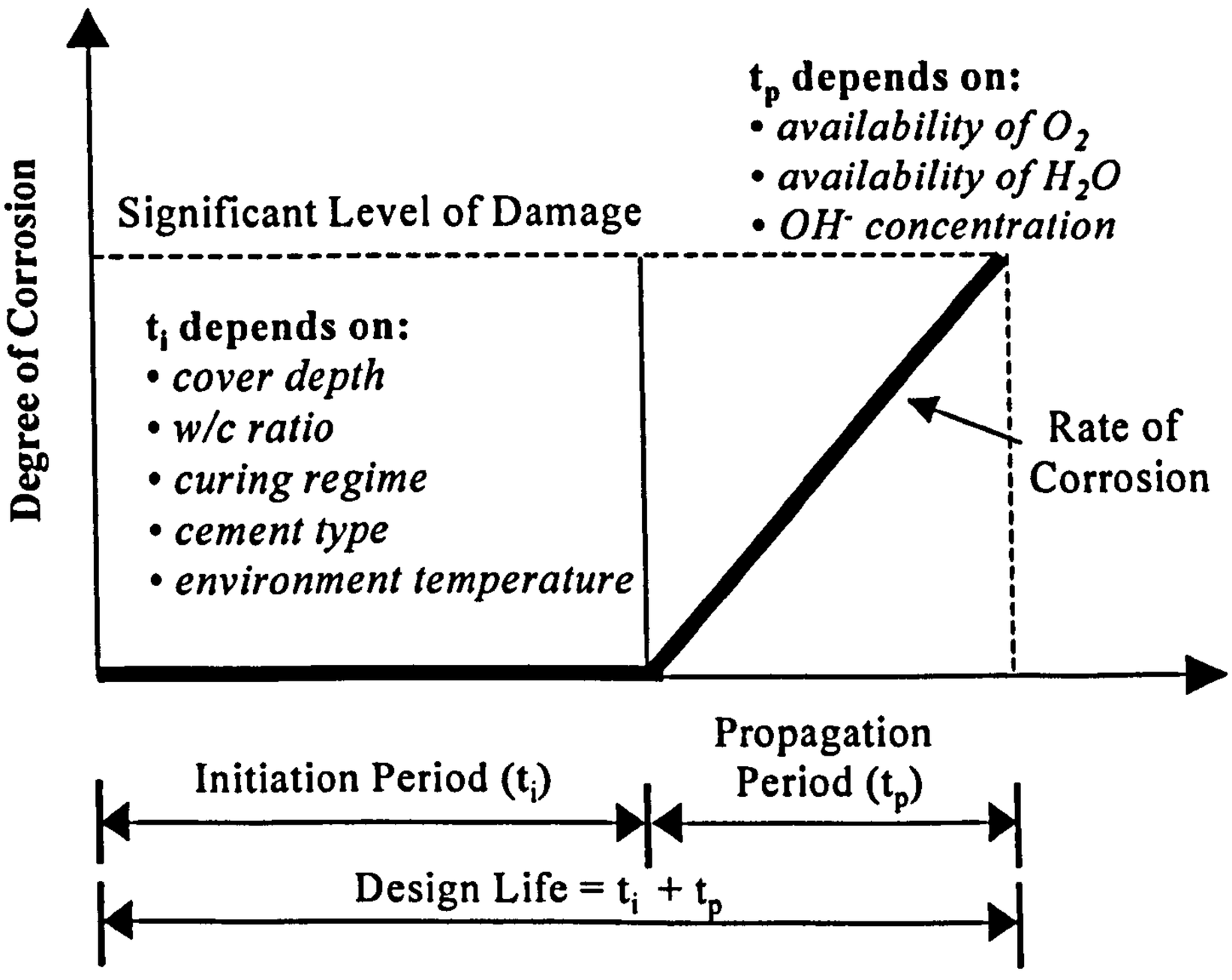


Figure 2.3 Principle of 'Design Life' as proposed by Tuutti (1982).

fluids causing a reduction in the concrete pH to between 8 and 9.5, the exact value being difficult to define (Gonzalez et al, 1996). At these relatively low pH values the passive γFe_2O_3 layer is no longer thermodynamically stable and the protective coating is destroyed allowing corrosion of the steel reinforcement and eventual spalling of the cover concrete.

2.5.3 Production of Durable Concrete Structures

The distinction between the production and placing of durable concrete, and the design and construction of structures which would be durable is well established (Somerville, 1986). The distinction is based on the fact that design specifications tried to solve the durability problem via a prescriptive materials approach and relatively ignored the fact that design, detailing and construction were at least as important in practice. Harrison (1993) identified five vital stages in the production of a durable concrete structure as shown in Figure 2.4. Production of a durable concrete structure begins at the design stage and is affected by all those involved in the design, specification and construction of the structure.

The requirements for good design, workmanship and construction practice is illustrated in De Sitter's "Law of Fives" (De Sitter, 1984, Cited CEB, 1992). Here, the decline and fall of a concrete structure is divided into the four phases shown in Figure 2.5. Unsatisfactory performance may begin in Phase A, due to a number of factors including bad design, poor material specification, and poor workmanship. Although reinforcement corrosion does not commence during Phase B, the carbonation front progresses towards the steel at a rapid rate during this phase. In the event that this progress can be identified, corrosion may be prevented by the application of a protective concrete surface coating or by electrochemical methods such as realkalisation. In Phase C, corrosion has been initiated at some points on the reinforcement bar and local spalling and rust staining is visible. Repair and maintenance has become necessary. If repair and maintenance are not implemented, the structure will reach a state in Phase D where major repair is necessary, including possible regeneration of structural integrity by replacing whole members.

De Sitter's Law of Fives contends that £1 spent on ensuring that the structure is designed and built correctly (Phase A) is equivalent to £5 spent on preventing further ingress of aggressive media towards the steel reinforcement (Phase B), £25 spent on local corrosion repairs(Phase C) and £125 spent in Phase D. It is not really important whether the law is based on threes, fours or fives, its purpose is to demonstrate the economic importance of achieving a sound design and good quality construction in the elementary stages.

2.5.4 Specification by Performance

The latest developments in concrete codes within Europe demonstrate a shift towards performance based specification. The key stages in the development of a performance specification are detailed in Table 2.2.

However, to achieve a reliable and economic performance specification for concrete requires a strategic initiative to co-ordinate current activity and to instigate the work needed to bridge the gaps (Harrison, 1995).

The unambiguous definition of the 'End of Service Life' or 'End of Design Working Life' is of major importance in the development of a performance specification and may include (Harrison, 1995):

a) start of corrosion of steel reinforcement;
b) first cracking of concrete due to steel corrosion (visible only with magnification);
c) cracking visible to the naked eye (approximately 0.1 - 0.2mm);
d) first signs of spalling;
e) excessive deflection;
f) collapse under the design loading

For the purposes of carbonation induced corrosion, the most likely criterion to be adopted is that of c), where cracking of the concrete is visible to the naked eye. This is a reasonable definition as the end of the service life or minimum intended working life of the structure since the client would probably become concerned about the residual life of the structure at this point (Harrison, 1995).

The establishment of limiting performance criteria during the life of a structure has been identified as essential to performance based specifications (Somerville, 1999) and must be on two levels:

1. A requirement which deals with the in-service time factor - possibly a target somehow expressed in terms of 'life'.
2. A requirement which directly relates to a minimum acceptable technical performance over that life.

CONCEPTUAL DURABILITY DESIGN

Specification of: *adequate cover and concrete quality*

OR

1. Redesign to move element out of aggressive conditions eg place frame of building behind cladding.
2. Redesign to reduce number of problem areas eg joints.
3. Redesign for shorter notional design life - provide for easy replacement of elements.

DETAILING OF ELEMENTS

1. Ensure elements are buildable - reduce reinforcement congestion and complicated sections.
2. Avoid collection of run-off water.

SPECIFICATION OF MATERIALS

1. *Water/cement ratio* - knowledge of relationships for different cement types.
2. *Cement Content* - minimum cement content.
3. *Cement Type* - knowledge of long term performance of various cement types in EN197-1.
4. *Fines Content* - sufficient content to fill gaps between coarse aggregate.
5. *Concrete Grade* - minimum for structural purposes.
6. *Concrete Mix Proportions* - workability and stability to ensure easy handling, placing and compaction.

EXECUTION / WORKMANSHIP

Ensure:

1. Proper handling and placing of mix
2. Compaction is adequate.
3. Specified cover depth is achieved
4. Concrete is cured to reduce loss of moisture

MAINTENANCE

Careful monitoring of structure and identification of problems at early stage.

Figure 2.4 Stages in the production of a durable concrete structure (After Harrison, 1993).

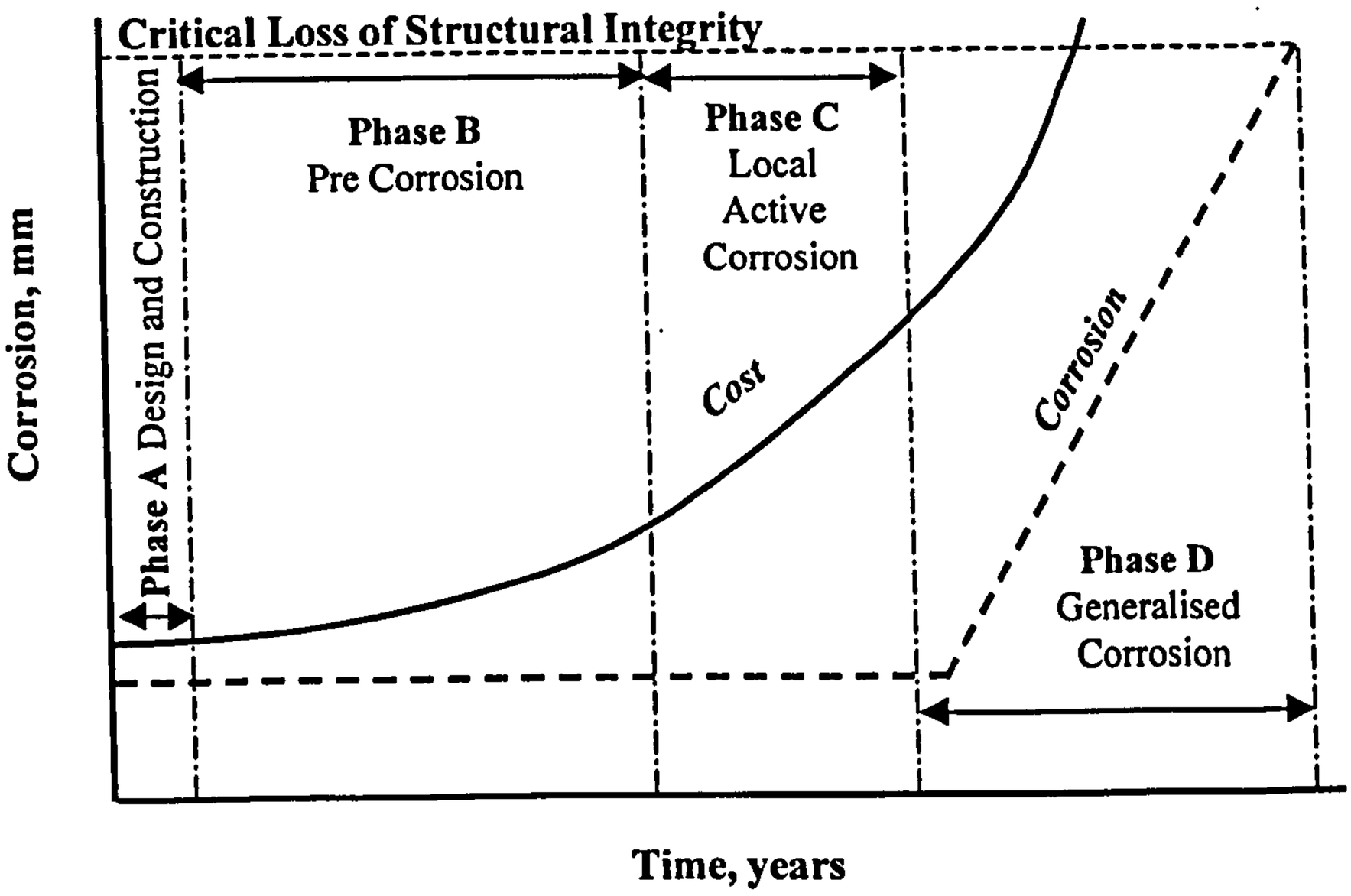


Figure 2.5 De Sitters Law of Fives (CEB, 1992)

Table 2.2 Seven stages in the development of a performance based specification (Harrison, 1995)

Stage	Notes
1. Exposure Class	Defining Exposure Classes with respect to a form of deterioration.
2. Design Methodology	Develop a quantitative design method and a definition for the end of the design working life.
3. Test Procedures	Develop test methods that relate to the output parameters of the design method. Develop sampling plans, precision statements and conformity procedures.
4. Provisional Conformity Requirements	From Stages 1 to 3 establish provisional conformity requirements. Check against traditional solutions.
5. Limitations of Test Applicability	Testing at the limits of concrete technology to confirm that adequate in service performance will be achieved. If not, limits on the materials that may be used will have to be introduced.
6. Production Control/ Acceptance Testing	Establishing effective systems for production control and acceptance testing.
7. Trials	Full scale trials and long term monitoring of the resulting structure to confirm the conformity requirements.

It has been argued that the definition of minimum acceptable performance criteria should ultimately focus on the transportation properties of the concrete as it is these properties which have a major effect on the durability of concrete (Hoff, 1999).

In order to judge the performance potential of a concrete, CEN identified that test methods must be developed in order to validate the performance of concrete within the defined exposure conditions (Delort, 1999). A Working Group was set up within CEN/TC51 and TC104 to select and study the existing test methods capable of making a clear distinction between concrete compositions and concrete constituents, eg: cements with regard to concrete durability (Delort, 1999). A number of deterioration mechanisms were identified, one being carbonation resistance. CEN developed a long term test and subjected this to a pan-European Round Robin, however, the results showed poor precision (CEN, 1992). One of the most important requirements of a performance test is that it will have adequate repeatability and reproducibility to give users confidence in the results and avoid disputes between testing parties (Delort, 1999).

2.6 DEVELOPMENT OF STANDARDS FOR CONCRETE SPECIFICATION

2.6.1 Background

The development of specification standards for concrete within the UK is shown in Table 2.3. For a number of years, concrete was specified by limiting values of bulk engineering properties such as water/cement ratio and compressive strength. In the 1950's a major breakthrough came with the provision of 'Exposure Classes'. These exposure classes were developed and eventually related to various concrete properties such as water/cement ratio, compressive strength, cement content, and cover depth (Concrete Society, 1999).

2.6.2 BS EN 206-1: Concrete: Specification, Performance, Production and Conformity

The development of the European code for concrete specification, BS EN 206-1 has been developed over the past 20 years and is although still in draft form, is due for publication in 2001 By 2003, it is intended that all concrete specified throughout Europe will be to BS EN 206-1. However, each European country will also have a National Application Document (NAD) to accompany BS EN 206-1. The NAD allows further specifications relevant to the countries' requirements.

Table 2.3 Summary of changes in requirements of concrete specification and relationships between concrete properties and exposure condition in British Standards (Concrete Society, 1999)

	1950/57 *CP114*	1959 *CP115*	1965 *CP116*	1972 *CP110*	1985 *BS8110*	1997 *BS5328*	2000 *BSEN206*
No. of Exposure Conditions	2	2	7	5	5	6	18
Concrete Property Linked to Exposure Conditions							
Concrete Grade	✘	✘	✔	✔	✔	✔	✔
Min Cement Content	✘	✘	✘	✔	✔	✔	✔
Max w/c ratio	✘	✘	✘	✔	✔	✔	✔
Cover Depth	✔	✔	✔	✔	✔	✘(1)	✘(1)

(1) Cover is specified in appropriate structural design standard

Table 2.4 Exposure class designations as defined in BS EN 206-1.

Class	Method of Attack	Example
X0	No risk of corrosion or attack	Concrete inside buildings with low humidity
XC	Corrosion induced by carbonation	Most exposed concrete structures
XD	Corrosion induced by chlorides other than from seawater	Bridges, highways car parks, swimming pools
XS	Corrosion induced by chlorides from seawater	Coastal structures, parts of marine structures
XF	Freeze-thaw attack	Highways, splash zones of marine structures
XA	Chemical attack	Foundations, industrial floors, tunnel linings

BS EN 206-1 has adopted the performance specification route with Exposure Classes being defined by each specific deterioration mechanism associated with concrete. Table 2.4 outlines the six exposure classes in BS EN206-1. Each Exposure Class is further divided into Class designations. Although informative examples are given within the standard it is up to the engineer to determine in which environment the concrete is likely to be built.

As this study is concerned only with the effect of carbonation, only Class XC will examined in more detail. The Class Designations for XC are as follows:

Class XC1 - Dry or Permanently Wet

This Class Designation was developed for concrete in which, although exposed to CO_2 in the surrounding environment or permanently exposed to water, carbonation induced corrosion will not occur. This is due to the fact that corrosion is a two phase process requiring both the ingress of CO_2 and O_2 in addition to the provision of moisture to assist in the corrosion process. The likelihood of carbonation induced corrosion in Class XC1 is very unlikely. Informative examples given are *concrete inside buildings with low humidity* and *concrete permanently submerged in water* (BS EN 206-1).

Class XC2 - Wet, Rarely Dry

Class Designation XC2 deals with concrete in an environment that is subjected to long periods of wetting, although it may be dry at some period during its working life. The corrosion activity in Class XC2 is, again, likely to be minimal as the conditions to support the ingress of CO_2 are not readily available over a long period. An informative example given is that *many foundations* (BS EN 206-1) may be valid within this exposure class as, due to fluctuating water tables, a concrete foundation may be saturated or dry over its working life.

Class XC3 - Moderate Humidity

The Class Designation XC3 is of great importance in carbonation induced corrosion. Exposure conditions in XC3 will have the required humidity levels to initiate corrosion of embedded steel whilst still allowing the ingress of CO_2 to neutralise the alkaline pore fluids in the cover concrete. Informative examples given are *concrete inside buildings with moderate or high air humidity* or *external concrete sheltered from rain* (BS EN 206-1).

Class XC4 - Cyclic Wet and Dry

As with Class XC3, Class XC4 will support conditions which will both promote CO_2 ingress and also provide enough moisture to initiate corrosion. The difference between XC3 and XC4

is the fact that XC4 deals with cyclic wetting and drying with the result that humidity levels within the concrete may fluctuate. The informative example given is *concrete surfaces subject to water contact, not within Exposure Class XC2* (BS EN 206-1). Class XC4 may provide for external concrete which is exposed to rain.

2.6.3 Recommendations for Concrete in BS EN 206-1 Exposure Class XC

BS EN 206-1 has adopted the performance specification route in recommending concrete properties within a given exposure. Table 2.5 details the recommendations given in BS EN 206-1 for concrete to be placed in Exposure Classes XC. The values given are based on the following assumptions:

i) The intended working life of the structure is at least 50 years, the minimum requirement given in ENV 1991-1 for building structures and other common structures.
ii) The cement type used is CEM I (Portland Cement) conforming to BS EN 197-1: 1998 with aggregate of maximum nominal upper size of 20-32mm.

Other permitted cement types have deliberately been omitted from BS EN 206-1 as many countries throughout Europe use a variety of different cements. Cement combinations in the European Standard for Cement, EN197-1:1998 are covered in each country's National Application Document. It is interesting to note that cover depth to embedded steel is not dealt with in BS EN 206-1, the specifier being referred *to ENV 1992-1 Eurocode 2: Design of concrete structures. General rules for buildings* which states provisions for minimum allowable cover depths.

2.6.4 BS8500 - Concrete: Complimentary British Standard to BS EN 206-1

The National Application Document, BS 8500 (BSI, 2001) is the UK complimentary British Standard to BS EN 206-1. BS8500 must be used in conjunction with BS EN 206-1 and contains the additional provisions where required and permitted. Although still in draft format, BS 8500, together, with EN206-1, will supersede BS 5328 , the current British Standard for Specification of Concrete in the UK, in 2003.

Table 2.6 shows the limiting values recommended by BS 8500 for Exposure Classes XC. There are four main fundamental differences between the recommendations made in EN 206-1 and BS 8500:

i) Class Designations XC3 and XC4 are merged in BS 8500

Table 2.5 Recommended limiting values for composition and properties of concrete for an intended working life of at least 50 years in BS EN 206-1.

	Class Designation			
	XC1	**XC2**	**XC3**	**XC4**
Minimum Strength Class	C20/25	C25/30	C30/37	C30/37
Minimum Cement[(1)] Content (kg/m³)	260	280	280	300
Maximum w/c ratio	0.65	0.60	0.55	0.50

[(1)] Cement type is CEM I conforming to BS EN 197-1:2000
NOTE: Minimum cover depth is taken from ENV 1992-1

Table 2.6 Recommended limiting values for composition and properties of concrete for an intended working life of at least 50 years in BS 8500-1.

	Class Designation					
	XC1	**XC2**	**XC3-4**			
Minimum Cover to Reinforcement (mm)	≥15	≥25	35	30	25	20
Minimum Strength Class	C20/25	C25/30	C25/30	C28/35	C32/40	C40/50
Minimum Cement Content (kg/m³)	240	260	260	280	300	380
Maximum w/c ratio	0.70	0.65	0.65	0.60	0.55	0.45
Permitted Cements and Combinations	See[(1)]	See[(1)]	As [(1)] excluding IV/B and combinations with more than 35% fly ash			

[(1)] CEM I, II/D, II/A-L, II/A-LL, II/A-Q, II/B-Q, II/A-S, II/B-S, II/A-V, II/B-V, III/A, III/B, IV/B to prEN 197-1

ii) Minimum strength classes have been adjusted to take account of standard UK strength class designations by cube strength rather than cylinder strength.

iii) Recommendations are for number of cement types from BS EN 197-1, not just CEM I.

iv) BS 8500 allows a 'trade-off' between cover depth and concrete grade, allowing a lower cover depth than the minimum stated in ENV 1992-1.

Class Designations XC3 and XC4 have been merged as it was felt that within the UK, these two exposure classes would cover the majority of situations where structural concrete would be subjected to carbonation induced corrosion (Harrison, 1998). The adjustment of the strength classes within BS 8500 has been made so that the cube compressive strength reflects standard specified strengths more common within the UK, ie: Grade C35 rather than C37.

Perhaps the most important difference is that BS 8500 allows a trade off between cover depth and concrete strength. This is also reflected in the maximum water/cement ratio and minimum cement content allowed.

2.6.5 BS EN 197-1 Common Cements- Composition, Specifications and Conformity Criteria

The introduction over the past 20 years of new materials which may be included in concrete has led to the development of a new European Standard, BS EN 197-1. Although still a DD EN, the standard has immediate implications for every European country as it will, in conjunction with the relevant NAD, allow larger number of binary cement types to be used with over 25 available in BS EN 197-1. Around 10 of these are common to UK engineers, however, the long term performance of a number of these binary cement types, including silica fume and metakaolin, is relatively unknown and the resultant confidence in using these materials is low (Harrison, 1994). A comprehensive study of unfamiliar cement types has recently been carried out at Dundee University (Williamson, 2000, Chaipanich, 2000) and a number of these cements were found to give 'unsatisfactory' performance in certain carbonating environments.

2.7 EFFECT OF MICRO AND MACRO CLIMATE ON CARBONATION

2.7.1 Temperature

The speed of the chemical reactions that occur during carbonation will be increased with an increase in temperature. Given the fact that carbonation is essentially a 3 three stage process, temperature will mainly influence Stage 2, the reaction of CO_2 with the pore fluids and

subsequent reaction with portlandite (Papadakis et al, 1990). The local macro climate will play a significant part in the carbonation of concrete. In countries with higher temperatures higher rates of carbonation of concrete will generally be experienced, providing other environmental factors, such as relative humidity, are similar. In Singapore, 59 year old structures showed much higher depths of carbonation compared to similar concrete structures in the UK (Roy et al, 1996). This was attributed to the higher temperatures associated with Singapore.

2.7.2 Relative Humidity and Exposure to Moisture

A number of studies have showed that the rate of carbonation is reduced in concrete with very low or very high moisture contents (Verbeck, 1958, Houst, 1993, Weirig, 1984). Indeed, the above studies reported that a maximum rate of carbonation was found at a relative humidity somewhere between 50% and 70%.

Ingress of atmospheric CO_2 and the subsequent carbonation mechanism is dependent on a number of factors, although the internal moisture condition of the concrete is very significant. It is unlikely that concrete which is fully saturated will carbonate since atmospheric CO_2 cannot progress into the concrete pores. Likewise, concrete with a high relative humidity will be very unlikely to carbonate as CO_2 will physically be unable to progress into the concrete. Very low internal relative humidity will also reduce the carbonation rate as the process requires the presence of some moisture to enable the penetrating CO_2 to react.

In structural reinforced concrete, the relative humidity and exposure to moisture is of vital importance as it will not only influence the carbonation process but also the corrosion of embedded steel (Parrott, 1991). Many laboratory based carbonation studies were undertaken in conditions where corrosion was unlikely to occur ie temperature of 20°C and a relative humidity of 65% (CEN, 1997). It is interesting to note that 'optimum' moisture conditions for carbonation and corrosion are quite different. Carbonation prefers a relative humidity somewhere between 50% and 70%. Although it has been found that corrosion can occur at a relative humidity of between 50% and 70%, the rate of corrosion is very low. A more rapid corrosion rate will only occur at a relative humidity of ≥75% (Dhir et al, 1993, Gonzalez et al, 1996).

In real structures, the exposure conditions of concrete elements may be broadly categorised as:

i) Indoors Exposure - Concrete inside buildings

ii) Outdoors Sheltered - Concrete which is externally exposed but sheltered from the effects of precipitation.

iii) Outdoors Unsheltered - Concrete which is externally exposed and unsheltered from the effects of precipitation.

It is exposure conditions ii) and iii) which are of concern where carbonation induced corrosion may occur since the environmental conditions, in terms of relative humidity and exposure to moisture, will support both carbonation and corrosion (CEN, 1997). The overall micro and macro climate in outdoor sheltered and outdoor unsheltered concrete will vary geographically and this variation is a determining factor on the process of carbonation and carbonation induced corrosion and, indeed, the design life of a concrete structure (CEB, 1992).

2.7.3 Atmospheric CO_2 Concentration

The level of atmospheric CO_2 is, on average 0.034% or 340ppm (Ahlbeck, 1998). This may increase to levels of close to 1000ppm over areas of high energy output such as cities (Pidwirny, 1999). Since 1800, the average level of atmospheric CO_2 has risen by 20% and by the year 2015, the level of CO_2 is projected to be 0.05% (Ahlbeck, 1998). The causes of this rise are manifold and environmental summits have lead to targeted reductions in CO_2 emissions.

The rate of carbonation of concrete is know to increase with an increase in the partial pressure of atmospheric CO_2 (Loo et al, 1994, Ho and Lewis, 1987). A number of researchers have carried out carbonation testing in CO_2 enriched atmospheres, a summary of the findings of which is given in Table 2.7. In all cases an increase in the level of CO_2 concentration increased the rate of carbonation, although this effect decreased with increasing concrete grade (Loo et al, 1994).

Few attempts have been made to correlate accelerated carbonation exposure results to natural carbonation exposure, mainly due to problems associated with differences in exposure period, CO_2 concentration, temperature, relative humidity and pre-conditioning of specimens. Table 2.8 summarises the most common interpretations made thus far by Dhir et al (1989b), Ho and Lewis (1987), and Ohga and Nagataki (1989). There is a general consensus that 1 weeks exposure in an accelerated carbonation environment of typically 4% CO_2 correlates to

Table 2.7 Accelerated environments adopted by different researchers.

Reference	Temperature, °C	RH,%	CO_2 Concentration, %
Ho and Lewis, 1987	23	50	4
Morinaga, 1990	30	60	5
Dhir et al, 1989b	20	50	4
Papadakis et al, 1991	20	65	50
Loo et al, 1994	30	65	12
Basheer et al, 1994	20	65	20
Müller, et al 1995	20	65	3
BRE, 1996	20	65	4

Table 2.8 Correlation between accelerated testing and normal exposure (Chin et al, 1992).

References	Long term exposure test	Accelerated test
Dhir et al 1989b	15 months outdoors sheltered	1 week, 20°C, 50% RH, 4% CO_2
Ho & Lewis 1987	1 year 23°C, 50% RH indoors	1 week, 23°C, 50 % RH and 4 % CO_2
Ohga and Nagataki, 1989	2,5,10,15 years indoors	0.56,1.4,2.81,4.21years,40°C, 50 % RH 7%CO_2

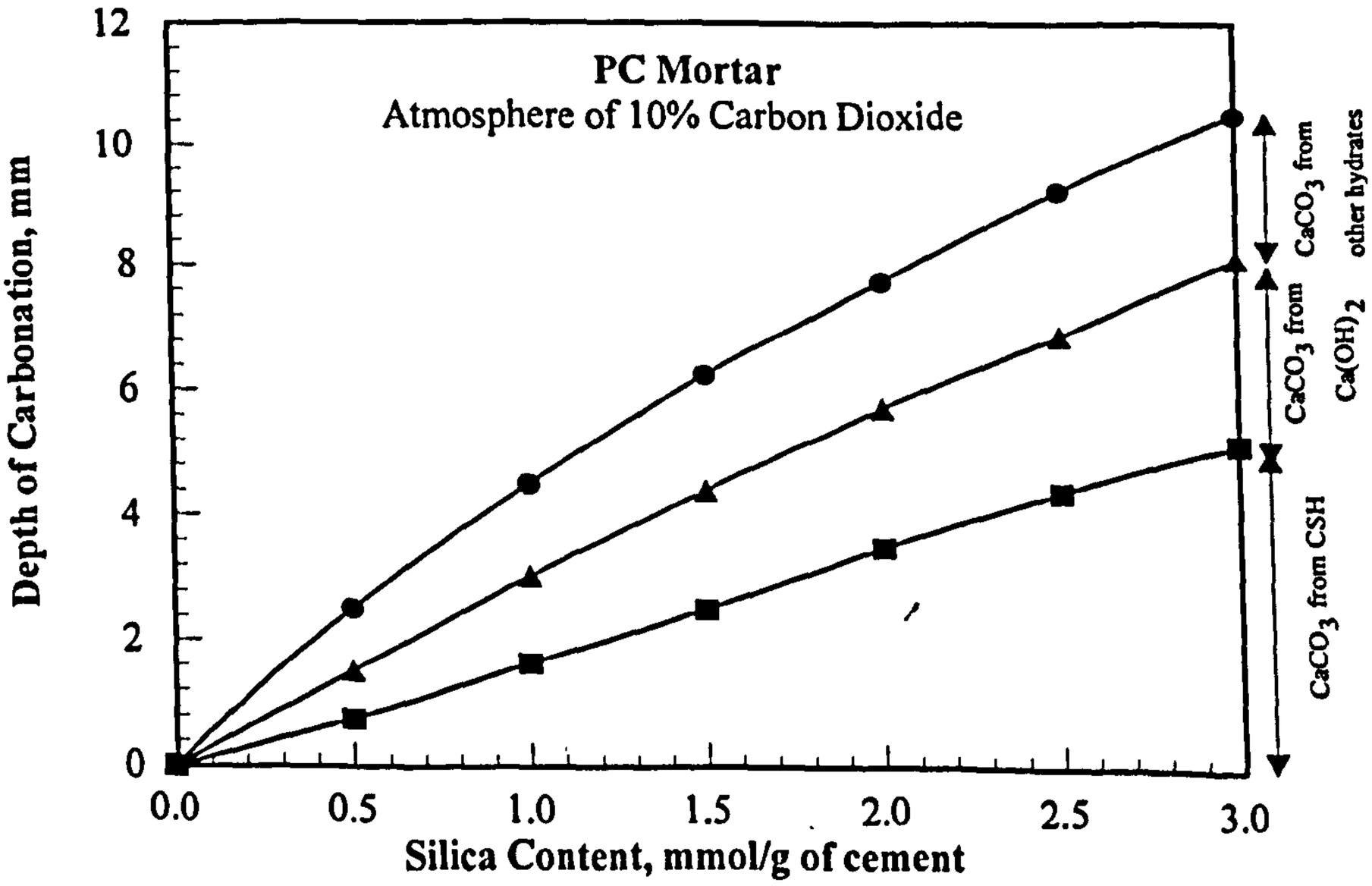


Figure 2.6 Increasing conversion of CSH to carbonate with increasing silica content in an accelerated carbonation environment (Matsusato et al, 1992).

1-1.5 years natural exposure. This is a very general correlation as exposure conditions are not exactly like for like.

Richardson (1988) stated that the chemical reactions associated with these accelerated test methods differ to those of natural carbonation exposure. In CO_2 rich atmospheres the formation of bicarbonates may occur which, in turn, leads to the production of further carbonates as the carbonation reaction proceeds into the concrete.

Destruction of the calcium silicate hydrate (C-S-H) was also observed by Matsusato et al (1992). Figure 2.6 illustrates that as the silica content of the concrete mix increases due to hydration, the conversion of the C-S-H to calcium carbonate increases in an atmosphere with a CO_2 partial pressure of 10%.

2.8 EFFECT OF CEMENT TYPE

2.8.1 Production and Historical Background

Pulverised-Fuel Ash (PFA)Concrete

PFA is an inorganic material formed from the combustion of finely ground coal (typically up to 75μm) to produce electricity. Temperatures of around 1500°C immediately burn off the carbonaceous content of the coal leaving a material consisting mainly of silica, alumina and iron oxide (Dhir, 1986). This material melts whilst in suspension and, on rapid cooling during removal with flue gases, forms a fine spherical particle material.

The first study undertaken on PFA in 1914 identified the key material characteristics. Davies et al produced the first comprehensive investigation into the use of PFA in concrete in 1937 (Davies et al, 1937). The inclusion of PFA in a number of concrete structures led to the development of standards for the material. The Lednock Dam in Scotland was the first major concrete structure in the UK to incorporate PFA and, to date, PFA has been used in many high profile projects worldwide such as the Channel Tunnel, the Storebaelt Link in Denmark and the Thames Barrage.

Metakaolin (MK) Concrete

Metakaolin is produced by calcining kaolinte clay at a temperature of between 700°C and 800°C (Murat, 1983, Ambriose et al, 1994). Kaolinte clay is more commonly used in the production of bone china and as a filler material in paper and paint. Although MK is not

strictly a waste material it is a by-product of the china-making and paper-making industry, being made from material which is unsuitable for use in making china or paper (ECC, 1996).

Metakaolin was first used in Brazil in 1965 for mass concrete (replacing 30% of cement) and structural concrete (replacing 20% of cement) (Saad et al, 1982). In the UK, the material is relatively 'new' and uses have been restricted to culverts, sumps and pipe sections. However, in the early 1990's, MK was used in foundations where 15% of PC was replaced (Asbridge et al, 1996) and more recently, MK has been used as a repair material on motorway bridges (May, 1999).

Condensed Silica Fume (CSF) Concrete

Condensed Silica Fume is a mineral compound which is a by-product of the ferrosilicon and silicon alloy industries (FIP, 1988). The process involves the reduction of high purity quartz in electric-arc furnaces heated to 2000°C with coal, coke and wood chips as fuel. CSF originates from the condensation of SiO vapour which mixes with oxygen in the upper furnace and oxidises. The material then condenses in the form of microspheres (Elkem, 1995).

The material was first used in concrete in the 1950's in a Norwegian tunnel segment and the first standards were published in 1975. However, it was not until the late 1970's and 1980's that the true effects on concrete properties were realised (Gjorv and Loland, 1986). From the construction of the New Tjorn cable stayed bridge in Sweden in 1981, silica fume has been used in many countries (Khayat and Aitcin, 1993) and there is now a draft European standard for the use of silica fume in concrete pr EN 13263(1998).

2.8.2 Chemical and Physical Characteristics

A comparison of typical chemical characteristics of PFA, MK and CSF is given in Table 2.9. PFA is essentially an aluminosilicate glass which consists of silicate, alumina and to some extent, iron. It also contains some calcium, magnesium and alkali metals, as well as carbonaceous particulates which are present due to incomplete combustion within the furnace (Cripwell, 1992). Mineralogically, PFA exists in the form of glassy particles with possibly a small quantity of ash being present as crystals (Alonso and Wesche, 1991). The mineralogical composition of PFA is of primary importance to its pozzolanic reactivity (Cabrera and Hopkins, 1987).

MK is typically composed of silicon and aluminium oxides and has a low calcium oxide content (Ambriose et al, 1994). It has been shown to exhibit a high degree of pozzolanicity (Jones and Troy, 1992) although this is dependent on the original chemical composition of the kaolinite.

CSF is a mineral compound composed of ultra-fine solid, amorphous glassy spheres of silicon dioxide (SiO_2). The chemical composition is dependent on the furnace type, nature of the furnace burden, chemical composition of the quartz and coal (Rau and Aitcin, 1990). However, CSF is typically >85% SiO_2 (Malhotra and Mehta, 1996) and in the UK, the chemical composition is usually over 90% SiO_2 (Elkem, 1995).

Table 2.9 also shows typical range of fineness and specific surface area of materials. It is interesting to note the variation in fineness between PFA and MK/CSF. Fineness of PFA is a limiting factor in BS 3892:Part 2, 1992 (BSI, 1992) and BS EN450: 1999 (BSI, 1999). In these standards, fineness is expressed as the residue retained on a 45μm sieve and in the UK, typical values range from approximately 6% to 36% (Cabrera and Hopkins, 1987). MK and CSF are both very fine particulate materials with MK average particle size being around 2μm. CSF is much finer, having an average particle size of 0.1μm, making it in the region of 50 to 100 times finer than a typical PC (Parker, 1985, Malhotra and Mehta, 1996). The relative density of PFA, MK and CSF is, on average, very similar. PFA with a higher relative density was found to have a higher Fe_2O_3 content (Alonso and Wesche, 1991).

2.8.3 Effect on Fresh Concrete Properties

The inclusion of PFA in concrete allows a reduction in water demand. The relationship between water demand and PFA/cement ratio has been found to be almost linear (Berg and Kukko, 1991). Early research has shown that a reduction in water demand can been attributed to a number of factors including the loss on ignition of the PFA (Weirig, 1970, Lewandowski, 1983), particle shape and fineness (Wesche and Berg, 1981). The earliest reasoning behind the improved workability of PFA concrete was suggested as a 'ball-bearing' effect due to the spherical nature of PFA (Anon, 1954). PFA has also been found to reduce bleeding and improve mix stability of concrete, with lower bleeding values attributed to the 'blocking' effect of the fine PFA particles preventing water from rising to the surface (Jones and Troy, 1992).

Table 2.9 Typical chemical and physical characteristics of PFA, MK and CSF.

	Material		
	PFA[1]	**MK[2]**	**CSF[3]**
Chemical Characteristics			
Major Oxide Composition, % weight			
SiO_2	40-50	50-55	85-98
Al_2O_3	20-35	38-43	<1
Fe_2O_3	1-8	<1	<1
CaO	5-12	<1	<1
MgO	1-3	<1	<1-2
SO_3	<1	<1	<1
Loss on Ignition	1-8[4]	<1	<1
Physical Characteristics			
Fineness, % retained on 45µm sieve	1-70[5]	<1	<1
Specific Surface Area, m^2/kg	200-500	10,000-15,000	15,000-20,000
Relative Density	1.9-2.5	1.8-2.4	2.0-2.3

(1) Typical range of values for UK PFAs (Booth, 1994).

(2) ECC(1995)

(3) Elkem (1995)

(4) BS 3892:Part 1 1993 limits 7.0%. BS EN450 limits LOI to 5.0% auto controlled but allows an upper limit of 7.0% on a national basis.

(5) BS 3892:Part 1 1993 limits fineness to 12%. Part 2 limits to 60%. BS EN450 specifies a single upper limit of 40%

The water demand of MK concrete has been found to increase with increasing MK replacement level (Saad et al, 1982, ECC, 1995). In one workability study, slump was found to reduce from 40-50mm to between 10-15mm by using replacement of 15% by weight of MK (Sabir, 1997). This was attributed to the very fine nature and associated high surface area of the material. In addition, bleeding was found to reduce with increasing MK replacement up to a level of 50% (Saad et al, 1982).

As with MK, the fine nature and very high specific surface, of CSF increases the water demand of a concrete mix (Malhotra and Mehta, 1996; Nehdi et al, 1998, Toutanji, 1998). Toutanji (1998) demonstrated that a reduction in slump from 210mm to 50mm was achieved when adding 15% CSF. Mixes containing CSF were found to be more stable and had reduced bleeding (Loland and Hustard, 1981)

2.8.4 Hydration of Concrete Containing PFA, MK and CSF

PFA, MK and CSF are all pozzolanic materials which require the presence of calcium hydroxide to activate their hydration reactions (Ghosh and Pratt, 1981, Dhir et al, 1986, Gjorv and Loland, 1986, De Silva and Glasser, 1990, Kostuch et al, 1993;). The pozzolanic reaction of PFA involves the alumino silicate amorphous component reacting with the calcium hydroxide from the hydration of the Portland cement. The pozzolanic reaction can occur after a few hours mixing (Ghosh and Pratt, 1981), however, it is more significant after 28 days (Owens and Buttler, 1980). PFA was also found to physically disperse cement flocs exposing the surface area of cement grains to allow further hydration (Dalziel and Gutteridge, 1986). It has also been argued that the inclusion of PFA leads to a 'preferential hydration' of silicate phases within cement (Cabrera and Plowman, 1980). Soluble calcium and sulfur ions on the surface of the PFA may combine to form gypsum thus retarding the aluminate phase hydration.

Investigations have shown MK to be highly reactive. However, the degree of reactivity depends on the mineralogical characteristics of the raw kaolinte, crystalline state of the material and presence of impurities (Murat, 1983). Several studies of MK concrete hydration mechanisms reported that metakaolin reacts with water and calcium hydroxide produced from cement hydration to form calcium alumino silicate hydrates, C_2ASH_8, and calcium silicate hydratres, CSH(Turrizani, 1964, Murat, 1983, De Silva and Glasser, 1990,Kostuch et al, 1993).

The reaction of CSF incorporated in a concrete is mainly pozzolanic (Gjorv and Loland, 1986). The ultra fine particles react with the calcium hydroxide realeased during the hydration of cement and combine with the existing CSH (Gjorv and Loland, 1986).

The inclusion of pozzolanic materials such as PFA, MK and CSF reduces the alkalinity of concrete pore fluids. As pozzolans require calcium hydroxide to react with, the available $Ca(OH)_2$ in the concrete pore fluids produced by Portland cement is reduced. Many researchers reported that the calcium hydroxide levels in concrete were reduced with the inclusion of MK (Larbi and Bijen, 1991; Kostuch et al, 1993). A typical reduction of 0.5 pH units was found in a MK 20% concrete at 56 days (ECC, 1996). Moreover, the alkali metal ion concentration was found to be markedly reduced in MK concrete (Kostuch et al, 1993). The level of concrete pore fluid pH was also found to reduce with increasing CSF replacement levels, being more significant up to 28 days (Page and Vennesland, 1983). Gjørv, however argued that the pH level in SF concrete was still above 11.5 making the drop insignificant with respect to carbonation resistance (Gjørv , 1995).

2.8.5 Compressive Strength

The long term strength of PFA concrete is greater than that of a corresponding PC concrete. A study of two ten year old bridges designed to an equivalent 28 day strength, one constructed from PC and the other from PFA concrete showed that at 10 years the PFA concrete was approximately 35% stronger (Thomas, 1989). This was attributed to the fact that the pozzolanic reaction is most significant post 28 days. However, early strength gain is lower in PFA concrete up to 28 days (Lane, 1983, Dhir, 1986, Jones and Troy, 1992) mainly due to the fact that the concrete has a lower PC content compared to a normal PC mix.

Many studies have shown that although early age compressive strength is lower, the 28 day compressive strength of MK concrete is higher than PC concrete up to a replacement level of 30% (Ambriose et al, 1994, Caldorone et al, 1994, Sabir et al, 1996, Wild et al, 1996, ECC, 1996). At a replacement level of 10%, the 3 day compressive strength of MK concrete has been found to be slightly higher than that of PC (ECC, 1995). The presence of MK densifies the cement matrix and also reduces the thickness of the cement paste-aggregate interfacial zone affording a better bond with the aggregate (Larbi and Bijen, 1991). At replacement levels of above 30% MK, long term compressive strength has been found to be lower due to insufficient calcium hydroxide content to initiate the pozzolanic reaction (Bredy et al, 1989).

The inclusion of CSF in concrete is known to increase the compressive strength (Sellevold and Radjy1983; Bayashi and Zhou, 1993; Toutanji, 1998). A study by Carrette and Malhotra (1992) demonstrated that at similar w/c ratios, a10% silica fume addition to concrete showed a greater compressive strength than control PC at all ages, although the improvement was greater up to 28 days. The greater compressive strength afforded by silica fume has been attributed to both the denser microstructure and improved bond between coarse aggregate and cement paste, the latter being due to the fine particles of CSF within this transition zone (Sarkar, 1991). It has also been argued that the strong aggregate-paste bond is due to the absence of orientated calcium hydroxide in the transition zone (Sarkar, 1991).

2.8.6 Permeation Properties

The inclusion of PFA in concrete improves the long term permeation properties (Thomas and Matthews, 1992). Thomas and Matthews (1992) showed that as the PFA content increased, the beneficial effects of PFA on permeability were increased. The study also showed that poorly cured concrete containing PFA was significantly less permeable than equal strength PC concrete. Partial replacement of cement with PFA may give rise to a higher level of permeation at early ages due to the slower early hydration characteristics associated with PFA concrete (Dhir et al, 1985). At a PFA replacement level of 50%, it was observed that the concrete had a higher air permeability (Swamy, 1990, Thomas and Matthews, 1992). This was also seen in samples obtained from structures ageing between 10-30 years containing fly ash, (Thomas 1989 and 1990). It was observed that in the first few millimetres from the surface (0-10mm) a coarser pore structure develops in fly ash concrete, however, beyond 10mm this tends to convert into a more refined micro-structure, (Thomas 1989).

The inclusion of MK in concrete refines the pore structure and reduces the absorptivity properties of the concrete (ECC, 1995). The water absorption of MK concrete was found to reduce with increasing replacement level of MK up to a level of 25% (ECC, 1995). Similar effects were also seen in mortar with MK replacement. At a replacement of 20% MK, the water absorption was found to reduce from 1.02 $kg/m^2/s^2 \times 10^{-3}$ to 0.45 $kg/m^2/s^2 \times 10^{-3}$.

The inclusion of CSF has been found to considerably reduce permeability (Sellevold and Nilsen, 1987, FIP, 1988, Bayashi and Zhou, 1993, Chan and Ji, 1998). On average a 40% reduction in water sorptivity was found in concretes with a 20% CSF replacement, with the effect of CSF being more pronounced when water cured (Chan and Ji, 1998). The

improvements in permeation properties are attributed to the densified microstructure obtained by the inclusion of CSF in the concrete.

2.8.7 Analysis of Published Carbonation Data

A large amount of data has been generated from the past 40 years of research into carbonation. However direct comparisons are difficult due to variability across the data such as:

i) concrete mix constituents - cement type, aggregate type, mix proportions
ii) difference in curing regimes
iii) exposure conditions - relative humidity, temperature, CO_2 concentration
iv) length of exposure period

For the purpose of comparison of cement types within this study, a normalisation procedure was adopted based on the traditional $d=kt^n$ relationship associated with carbonation of concrete. The minimum intended working life of 50 years given in ENV 1992-1 includes both the time for the concrete to carbonate (initiation period) and time for steel to corrode (propagation period). A review of carbonation in UK structures showed that the initiation period was approximately 30 years (Parrot, 1997). A more conservative approach was adopted by Hobbs (1998) in which the initiation period was 35 years and the propagation period taken as 15 years. This conservative approach was adopted in the analysis of published carbonation data. The depths of carbonation are normalised to 35 years and compared on the basis of 28 day compressive strength. Parrot (1997) provided guidance on the 'n' value in the equation $d=kt^n$,depending on the level of exposure to moisture, and this is shown in Table 2.10. For the purpose of the analysis the author adopted the following values:

i) Indoor Concrete 'n' = 0.5
ii) Outdoor Sheltered 'n' = 0.4
iii) Outdoor Unsheltered 'n' = 0.3

An example of normalising a carbonation depth of 6mm in concrete exposed indoors after a period of 10 years is given below:

Step 1: Determination of 'k' in $d=kt^n$

$$6 = k \times 10^{0.5}$$

$$k = 1.9$$

Step 2: Determination of 35 year carbonation depth

$$d = 1.9 \times 35^{0.5}$$

$$d = 11.0mm$$

2.8.7.1 Effect of cement type on carbonation

Tests on PC concrete in three different climatic conditions showed that increasing the pore fluid level within the concrete reduced the carbonation rate. Figure 2.7 and Figure 2.8 show the results of UK laboratory based tests normalised to 35 years and compared on 28 day strength. It can be seen that outdoors unsheltered conditions give the lowest depths of carbonation.

An investigation into structures exposed in Kuwait showed coastal structures were found to carbonate more than those at 6-12 km from the coast, Figure 2.9, (Haque and Al-Khaiat, 1997). This was attributed to the dry environment in the region with the macro-climate at the coast favouring the progress of carbonation, a trend very different to that experienced in the UK.

A considerable amount of research has been carried out with respect to carbonation of PFA concrete (Hobbs 1988, Dhir et al 1989b, 1992, 1993, Kokubu and Nagataki, 1989, Ogha, 1989, Thomas 1989, 1990, Thomas and Matthews, 1992, Matthews 1994, 1995, Parrott 1996). A 20 year study on the corrosion of reinforcement embedded in concrete containing 30% PFA was carried out in Japan using three different binder contents namely 250, 300 and 350 kg/m³, (Kokubu and Nagataki, 1989). No corrosion was observed after10 years with covers of 30-50mm, however after 15 years, signs of corrosion started to appear on concretes with a binder content of 250 kg/m³.

A comparison is of PC and PFA concrete, designed to an equal w/c ratio showed PFA concrete exhibited slightly higher depths of carbonation (Matthews 1995). This was mainly attributed to the consumption of the $Ca(OH)_2$ by the PFA due to the pozzolanic reaction, however this is more noticeable at higher PFA replacement levels of 50% by mass of cement.

Figures 2.10 and 2.11 illustrate findings obtained from UK investigations into the performance of PFA concrete in laboratory tests subject to two different curing regimes, (Thomas and Matthews 1992, Barker and Matthews 1994, Hobbs 1994, Matthews 1994, 1995,). The normalised data shows that at 35 years, the carbonation depths of a 37 N/mm² concrete were

24 mm and 22 mm in an outdoors sheltered exposure following 1 and 3 day curing respectively.

High volume PFA with replacement levels of around 50% was used in constructing an area for stockpiling coal at the Didcot Power Station in 1981. Surveys made by Dunstan et al (1993) into the performance of the concrete showed depths of carbonation ranging between 2-11 mm at three different locations having equivalent cube strengths of 43.7-45.3 Mpa.

Figure 2.12 shows these results along with another survey made of four CEGB power stations, ageing between 10-30 years at the time of investigation, containing both PC and PFA, at Aberthaw, Pembroke, Poole and Ferrybridge.

Very little is reported about the performance of MK in carbonation. Figure 2.13 shows the performance of metakaolin concrete with replacements of 10 and 15% compared to a control PC designed to the same w/c ratio in 2 different environments, (BRE, 1996). The Figure shows that the carbonation depth tends to reduce as the concrete is subjected to cyclic wetting and drying.

In sheltered conditions, the PC concrete displays a lower carbonation depth than the MK concrete, however the difference between PC and increasing MK replacement in unsheltered conditions is very small indicating that concrete pore saturation levels may play an important role in carbonation resistance.

Due to its pozzolanic reactivity, CSF concrete carbonates at a faster rate than PC concretes at the same 28-day strength (Byfors 1985). Figure 2.14 plots long term laboratory data of CSF normalised to 35 years. As illustrated, the depths of carbonation increases with increasing CSF replacement.

It is very difficult to provide a strict comparison between the long term data of PFA, MK and CSF concretes as there are inevitable differences in mix constituents, curing regimes and compressive strengths. The relative novelty of MK and CSF mean that there is a limited amount of data available on the carbonation of these materials.

Table 2.10 Interpretation of n values from Parrott's 1994a classification.

Relative Humidity, %	***40***	***50***	***60***	***70***	***80***	***90***	***95***	***98***	***100***
n value	0.48	0.51	0.51	0.48	0.41	0.31	0.25	0.21	0.18
Exposure*	Indoors			Outdoors Sheltered		Outdoors Unsheltered		N/A	

* Author's interpretation for each environmental condition.

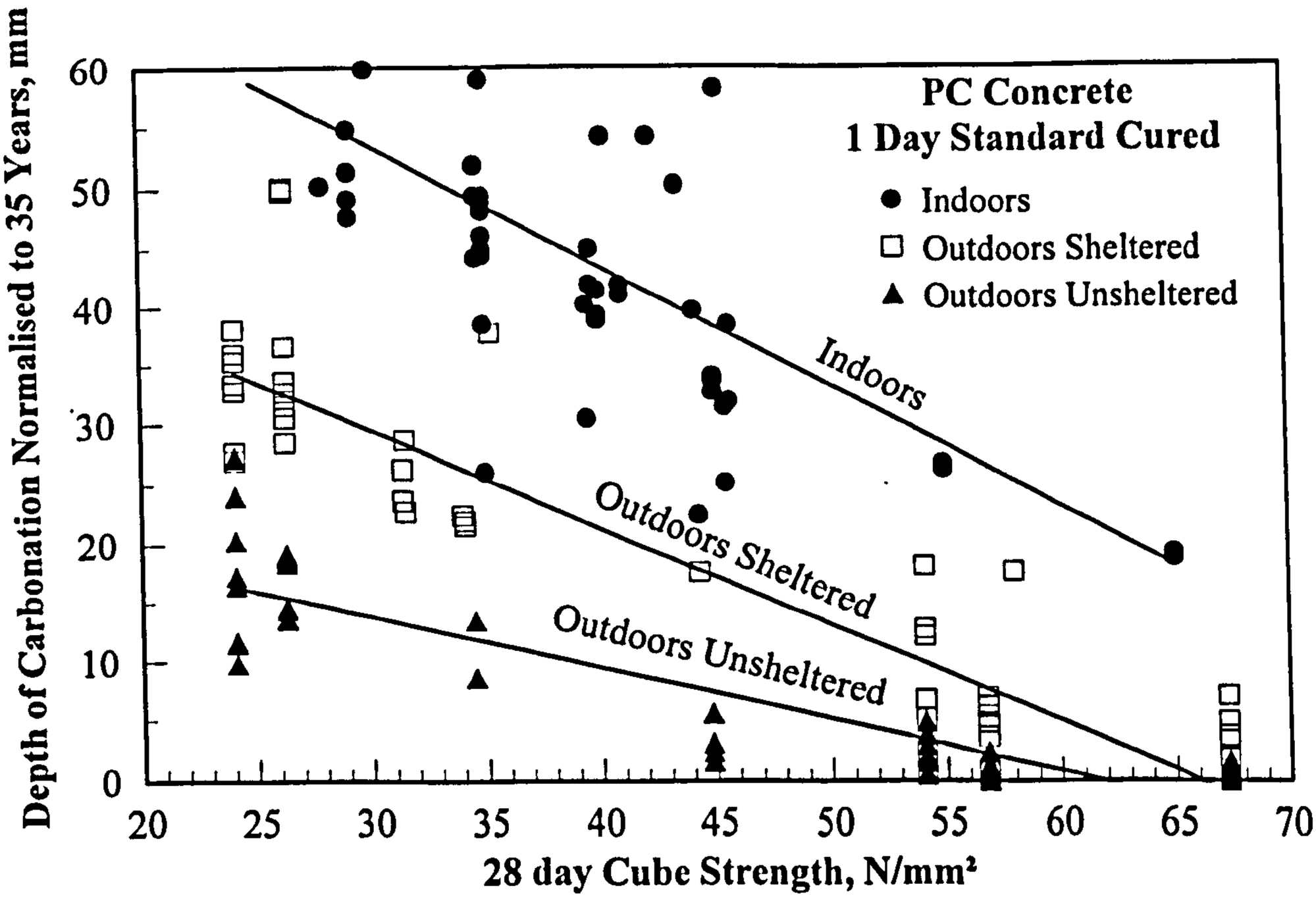


Figure 2.7 Relationship between normalised 35 year depth of carbonation and compressive strength for PC concrete 1 day cured (Dhir et al, 1989b; Thomas and Matthews, 1992; Barker and Matthews, 1994; Matthews, 1994, 1995; BRE, 1996; Parrot, 1996).

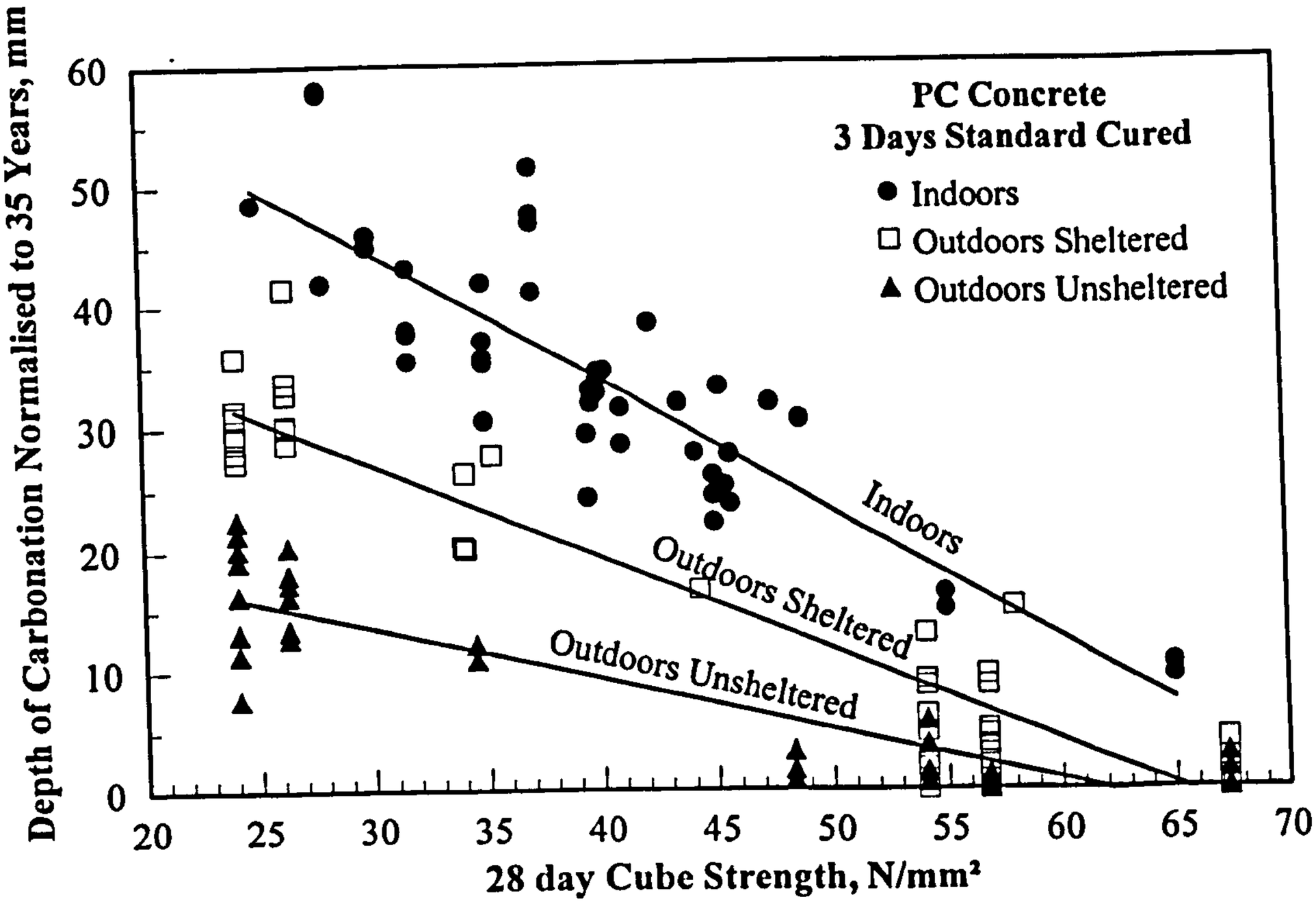


Figure 2.8 Relationship between normalised 35 year depth of carbonation and compressive strength for PC concrete 3 day cured (Ali and Dunster, 1998, Hobbs et al, 1998).

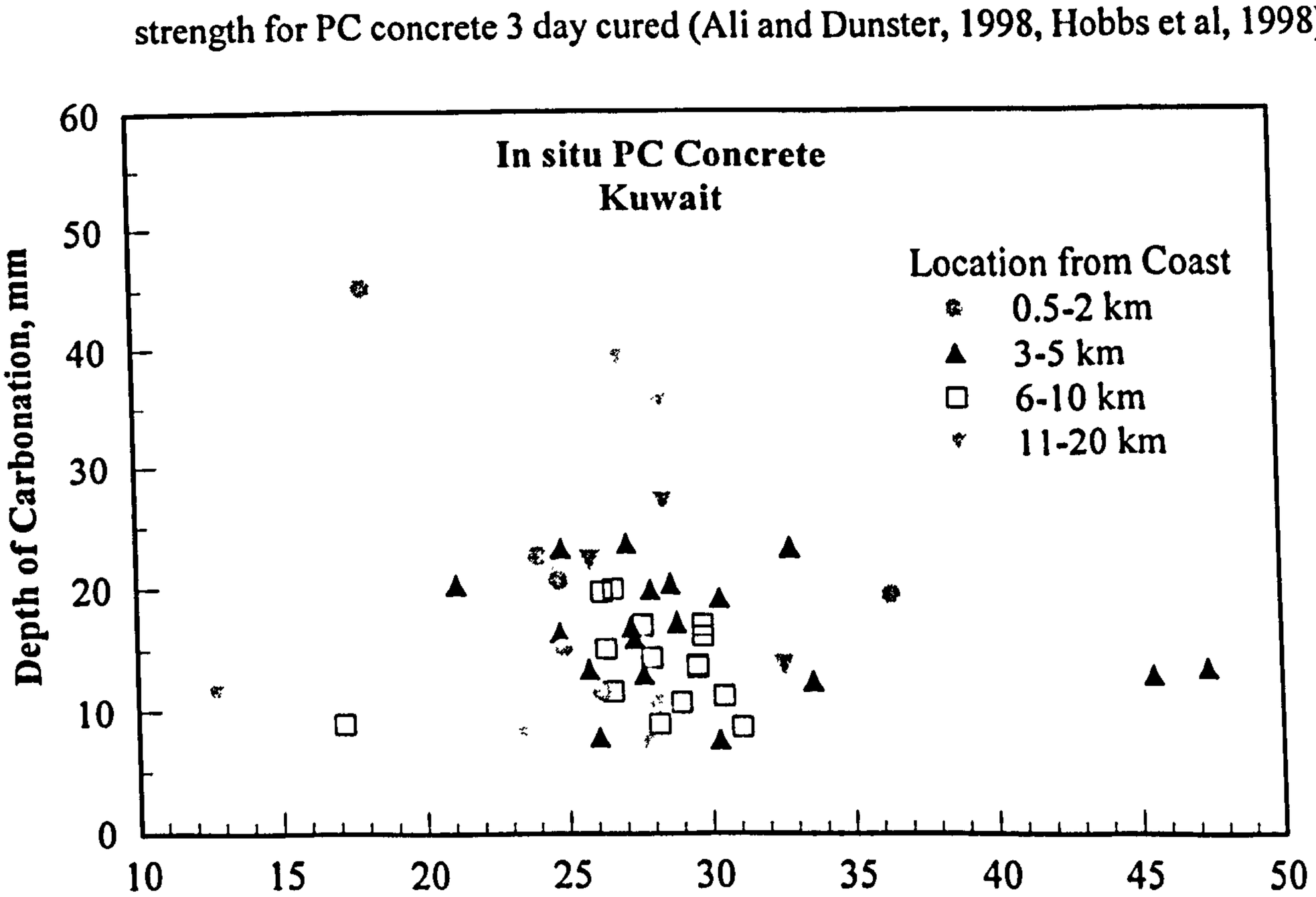


Figure 2.9 Relationship between normalised 35 year depth of carbonation and compressive strength of in-situ concrete in Kuwait (Haque and Al-Khaiat, 1992).

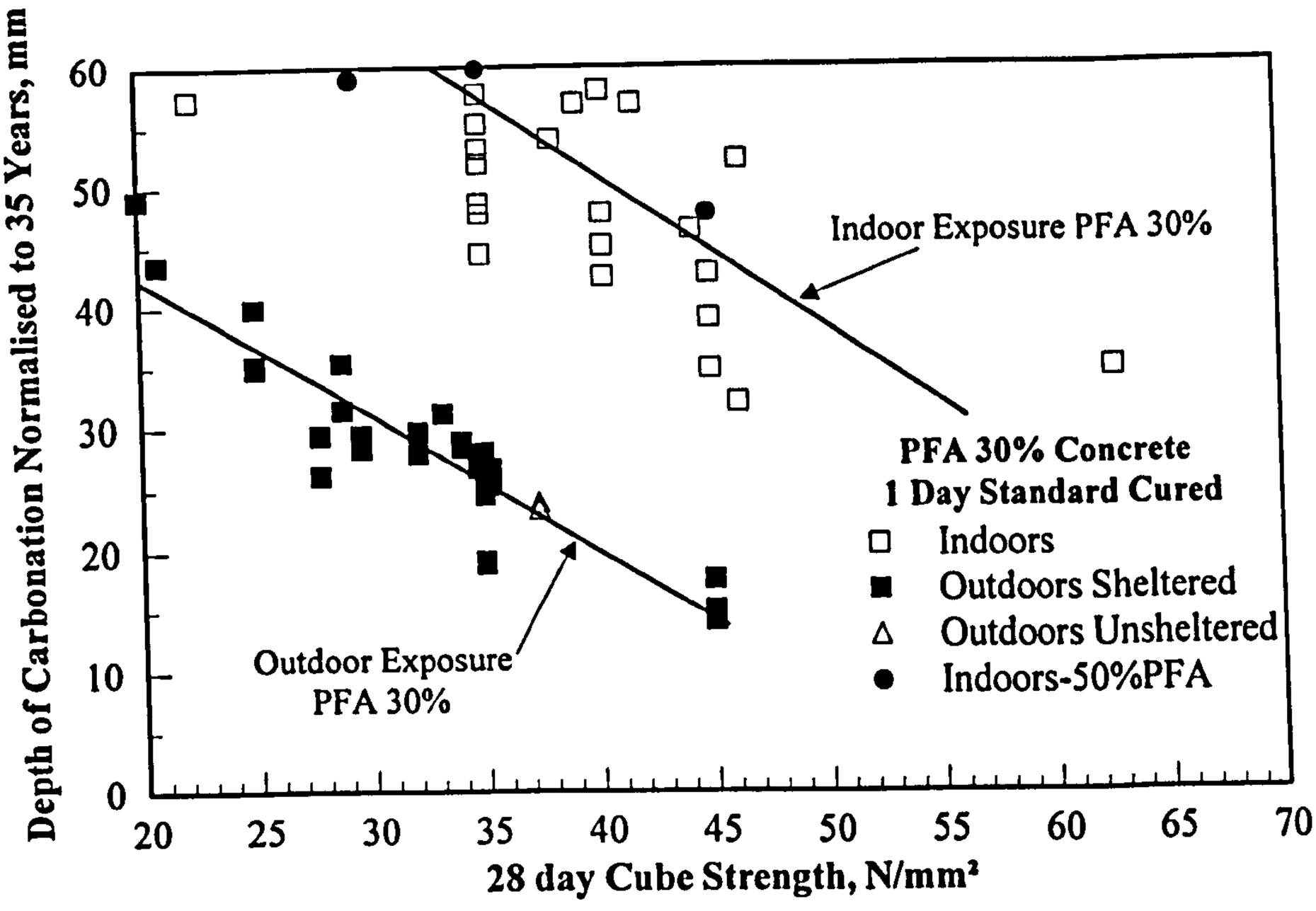


Figure 2.10 Relationship between normalised 35 year depth of carbonation and compressive strength PC/PFA 30% concrete, 1 day cured (Barker and Matthews, 1994, Hobbs, 1994; Matthews, 1994, 1995; Ali and Dunster, 1998).

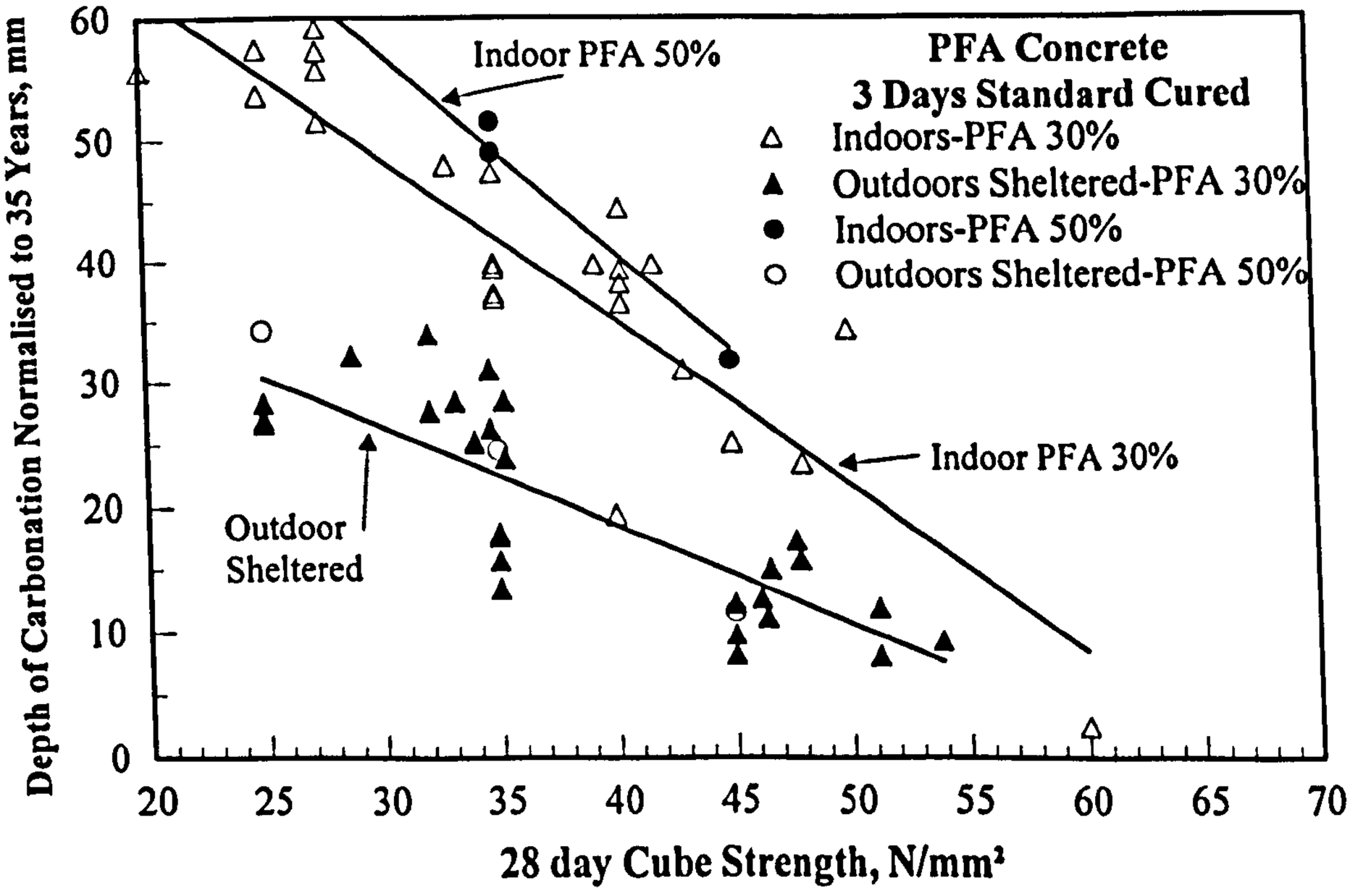


Figure 2.11 Relationship between normalised 35 year depth of carbonation and compressive strength PC/PFA 30% concrete, 3 day cured (Barker and Matthews, 1994, Matthews, 1994, 1995, Ali and Dunster, 1998).

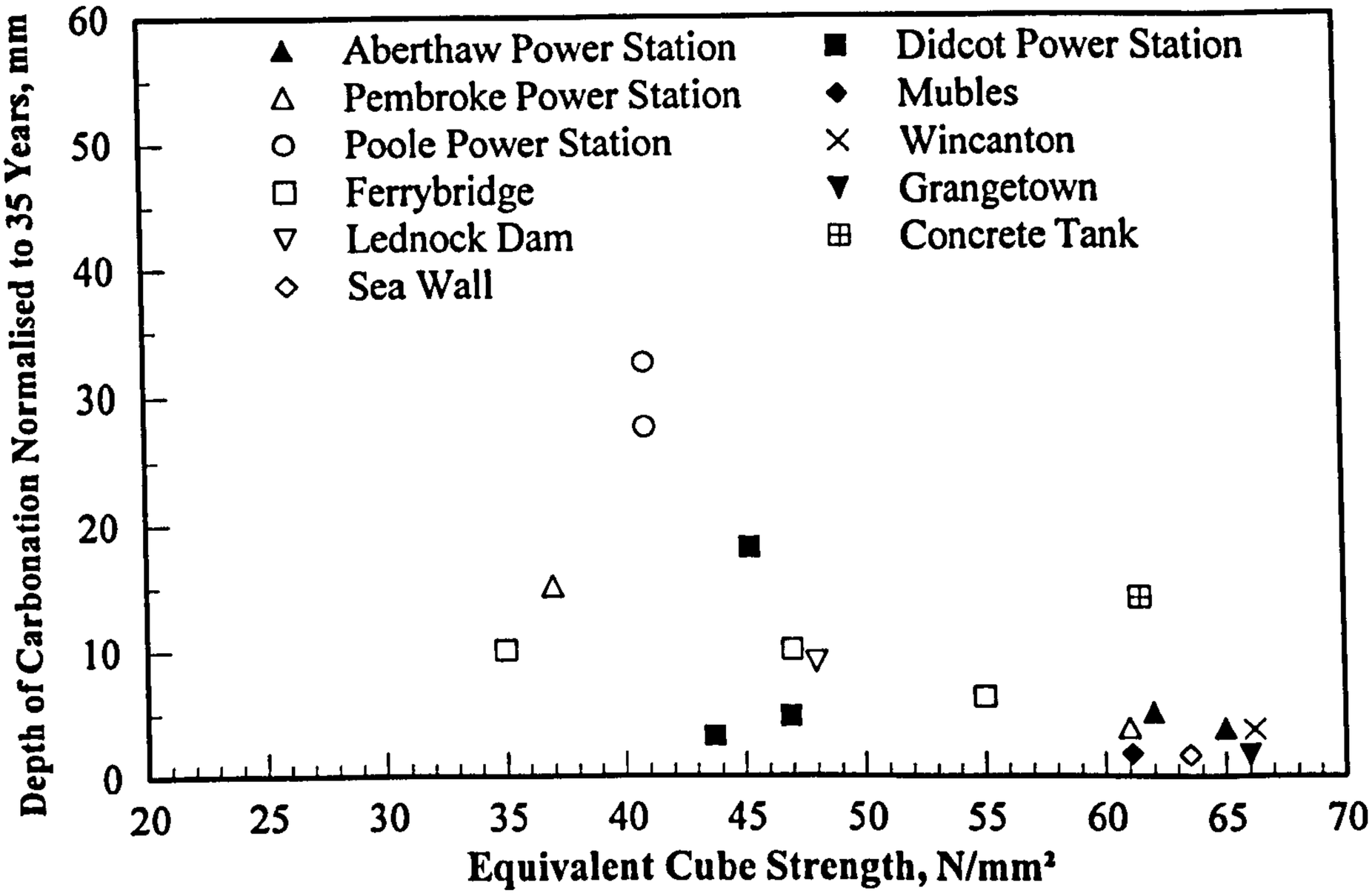


Figure 2.12 Normalised depths of carbonation from structures incorporating PFA (Thomas, 1989, 1990, Thomas et al, 1990, Dunstan et al, 1993, Newman et al 1983)

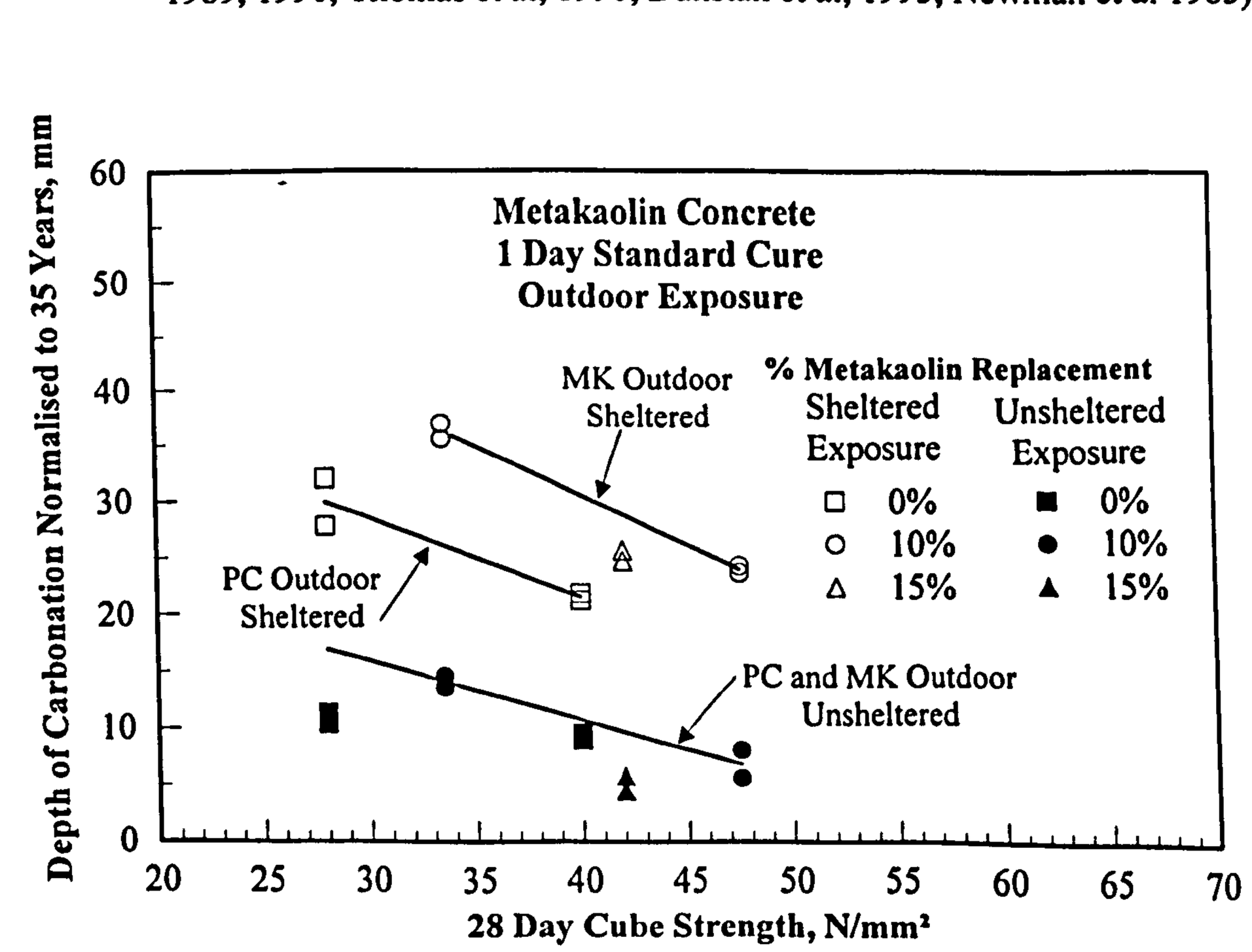


Figure 2.13 Normalised 35 year carbonation depths of MK concrete (Dunster, 1996).

Table 2.11 illustrates a tentative comparison of PC, PFA, MK and CSF concrete carbonation data after 1 day standard curing, normalised to 35years at a compressive strength of 37N/mm^2. A comparison across the three exposure types, indoor, outdoor sheltered and outdoor unsheltered, shows that PC concrete exhibits the lowest carbonation depth in all cases. However, as the exposure to moisture increases, the differences between the various cement types, especially PC, PFA and MK are reduced considerably indicating that the moisutre level of the concrete is paramount in the carbonation process.

Investigations in an accelerated CO_2 exposure of 4% CO_2 looked at the effect of different PFA replacement levels of 15, 30 and 50% (Jones 1994). Here, no significant differences between replacement levels of 15 and 30 % were noted but higher depths of carbonation were observed at a replacement level of 50 % PFA (Jones 1994).

In a 5% CO_2 rich atmosphere, the performance of silica fume at different replacement levels showed higher depths of carbonation compared to the control PC concrete compared on an equal compressive strength basis (Jones 1994, Haque and Al- Khaiat 1997). The depth of carbonation was also found to increase with increasing replacement levels and this was attributed to the nature of the pozzolanic chemical reaction between the hydrating PC and CSF (Yamato et al, 1989).

2.9 EFFECT OF AGGREGATE AND PARTICULATE FILLERS

It has been observed that with an aggregate size of 20 mm, the performance with respect to carbonation is not impaired in tests carried out in accelerated exposures (Dhir et al 1989b, Basheer 1991, Basheer et al 1994). Increasing the aggregate size to 40mm, results in an increase in the measured depths of carbonation (Dhir et al, 1989b). This is attributed to the poor particle packing associated with larger aggregates (Dhir et al 1989b, Basheer 1991, Basheer et al 1994).

Lower depths of carbonation are observed with higher aggregate contents (Basheer et al 1994) due to the increased tortuosity of the flow path resulting in a marked reduction in permeability. An optimum aggregate/cement ratio of 4.65 has been proposed (Basheer 1991, Basheer et al 1994).

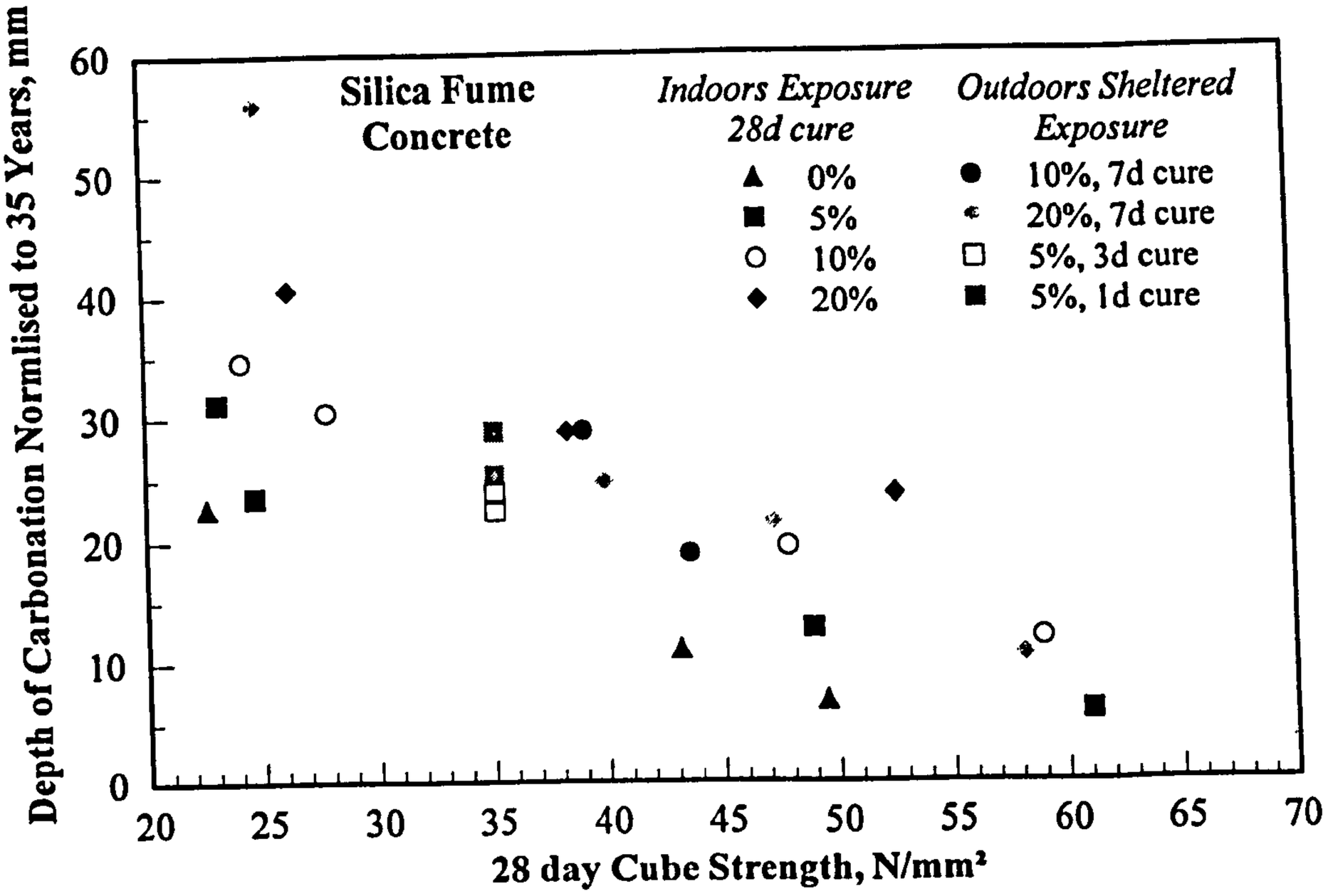


Figure 2.14 Normalised 35 year carbonation depths of CSF concrete subjected to different curing regimes and exposure conditions (Byfors, 1985, Ali and Dunster, 1998).

Table 2.11 Tentative comparison of long term published carbonation data normalised to 35 years at a 28 day compressive strength of 37N/mm².

	35 Years Normalised Depth of Carbonation of 1 Day Standard Cured 37N/mm² Concrete, mm			
	PC	**PFA 30%[1]**	**MK 10%[2]**	**CSF 5%[3]**
Exposure Condition				
Indoors	46	55	l.d.	l.d.
Outdoor Sheltered	24	25	32	30[4]
Outdoor Unsheltered	11	12	12	l.d.

(1) Increased replacement levels showed slight increase in carbonation depth.

(2) Increased replacement levels showed slight increase in carbonation depth. Notable reduction in carbonation depth with increasing exposure to moisture. Outdoor unsheltered conditions showed little difference between PC, MK10 and 15%.

(3) Increased replacement levels showed slight increase in carbonation depth.

(4) Data is for 35N/mm² concrete.

l.d. Limited published data available.

An investigation of mortars showed that, at low sand contents, the diffusion coefficient of CO_2 gas decreased. However, when the sand content was increased above 50% by volume, a steep increase in the CO_2 diffusion coefficient was observed, (Houst, 1993). This increase was attributed to the interconnection of interfacial zones upon increasing the sand volume in the mix thus increasing the zones of higher porosities, (Houst, 1993). A similar observation was made with concretes mixed with normal aggregates at a high aggregate/cement ratio (Papadakis et al 1990) In this case the increased depth of carbonation was attributed to a reduction in the molar concentration of $Ca(OH)_2$ and CSH in the cement paste.

Lightweight aggregate concrete is considered to be more permeable than normal dense aggregates and this results in increased depth of carbonation (Richardson 1988, BRE 1995). In-situ investigations of structures in the UK, yielded little evidence of reinforcement corrosion in good quality concrete made with lightweight aggregates (Mays and Barnes 1991). In addition, an investigation of concrete bridge decks located over sea water indicated depths of carbonation of less than 20mm after 35 years (Holm et al 1988). Furthermore, in a 10 year laboratory study, only lightweight concrete specimens exposed outdoors with a w/c >0.7 showed higher depths of carbonation than concrete made with normal dense aggregates (Swamy and Jiang, 1993).

There are currently two draft standards for the use of particulate fillers in concrete. prEN 12620, which specifies aggregate for concrete that contains filler, and a draft British Standard dealing with the use of ground limestone in combination with Portland Cement. BS EN197-1 recognises two types of limestone cement:

i) CEM II/A-L allowing 6-20% limestone
ii) CEM II/B-L allowing 21-35% limestone

The effect of adding a fine material to concrete is generally to increase the water demand of the mix (Neville, 1996). Additions of 5% limestone filler were found to require an increase in water content to achieve workability. This value increased with increasing limestone filler content, however, the effect of a fine filler on the rheology of concrete is very much dependent on its fineness, particle size distribution and particle shape (Nehdi et al, 1998). Brookbanks' (1989) comprehensive review showed that setting times were reduced by the inclusion of limestone filler and water demand was not significantly affected Long term strength was found to be slightly lower in limestone filled concrete and the inclusion of limestone as a filler has been found to reduce the sensitivity of concrete to curing (Matthews, 1994).

It has been suggested that the addition of $CaCO_3$ aids cement hydration by providing nucleation sites for the growth of hydrates (Moir, 1994, Kelham, 1998). It has also been found that the $CaCO_3$ may become incorporated into cement hydrates, although only a small amount (10-20%) have been found to react after 129 days hydration (Klemm and Adams, 1990; Pera et al, 1999).

Although practical experience of limestone filled concrete is limited within the UK, an Industry/BRE programme (BRE, 1989) concluded that the use of limestone filler did not significantly affect the carbonation resistance, with performance being similar to the reference PC mixes.

2.10 TESTING THE CARBONATION DEPTH OF HARDENED CONCRETE

The most common method for testing the carbonation depth of hardened concrete is by measuring the change in the concrete pH value (Parrot, 1987). The reduction in pH can be very sharp (Pihlajavaara, 1976), and the critical value at which the passivation of steel reinforcement is lost it typically around pH 9.0-9.5 (Gonzalez et al, 1996). From a range of common pH indicators, only phenolphthalein and thymolphthalein display changes in colour over this range (Parrot, 1990a). Of these, phenolphthalein displays a vibrant purple colour in areas of pH>9.8 which is readily visible on a concrete surface or powdered sample. Thymolphthalein is not readily visible on concrete making it's use unsuitable. A distinct advantage of the use of a sprayed indicator is the low cost, simplicity and adaptability for use on site (Bungey and Millard, 1996).

The main disadvantage of the indicator method is that it can only distinguish between a carbonated and non-carbonated (or neutralised and non-neutralised) zone. It has been argued that corrosion of embedded steel can be initiated before the actual carbonation front reaches the surface of the steel implying that the transition zone may be influential.

A number of test methods to determine the depth of carbonation in hardened concrete have been used and the more common methods are summarised in Table 2.12. Of these, thermogravimetric analysis (TGA) and X-ray diffraction (XRD) are the most common methods used. TGA allows determination of the transition zone between the carbonated and uncarbonated regions and can also quantify the amount of $Ca(OH)_2$. XRD is commonly used

to qualitatively analyse the products of carbonation, differentiating between the various types of carbonate formed.

2.11 ESTIMATING THE CARBONATION DEPTH OF CONCRETE

Carbonation involves the interaction of many parameters involving both concrete properties and the environmental conditions to which the concrete is exposed. Assumptions and conclusions have been reached that help simplify the mathematics involved, with various formulae and approaches proposed. These are mainly based on empirical methods and very few are founded on rigorous mathematical analysis involving the phenomenological aspects of the carbonation process (Richardson 1988).

2.11.1 Derivation of the $\sqrt{t}$ Equation

Many predictive equations have taken the form that the ingress of carbon dioxide into concrete is proportional to the square root of time (Richardson, 1988). This assumes that the movement of CO_2 into the concrete will follow Fick's laws of diffusion.

Equating the rates of both the chemical and physical processes occurring during carbonation, results in:

$$dq = DA\frac{|r - r_x|}{x}dt \tag{2.5}$$

where:

q = quantity of carbon dioxide diffusing through the concrete, kg
D = diffusion coefficient, m^2/s
A = area, m^2
r = concentration of the CO_2 gas at the surface, kg/m^3
r_x = concentration of the CO_2 gas at depth x, kg/m^3
t = time

Integrating the differential equation and solving for x with the assumption that the CO_2 concentration r_x at the depth of carbonation is zero yields:

$$x = \sqrt{\frac{2Drt}{c}} \tag{2.6}$$

where:

Table 2.12 Summary of commonly used test methods for determining the carbonation depth of concrete

Test Method	Method	Advantages	Disadvantages
Phenolphthalein	• Concrete samples broken off test element or drilled dust samples from insitu concrete. • Indicator is sprayed on the freshly broken concrete surface which is cleaned of dust and loose particles or dust sample. • Saw-cut surfaces are not recommended. Upon contact with the indicator, areas containing calcium hydroxide change colour to dark purple • Areas with an abundance of $CaCO_3$ remain colourless.	• Gives distinct colour difference between carbonated and non-carbonated regions • Reliable within an accuracy of 0.5 mm • Reproducible • Not user sensitive • Favoured and adopted by most standards and researchers • Requires minimal amount of material • Easy to use • Can be used on site	• Tends to produce lower carbonation fronts compared with other complex analyses • Does not distinguish between carbonation and sulfatisation • Moisture flow of lime saturated water through carbonated zones can produce an erroneous purple image • Pore solution containing potassium and sodium hydroxide are reported to buffer the solution in carbonated concrete to pH levels high enough to cause red colouration of the indicator • Troublesome to use with white cement • May produce calcium hydroxide on exposure to atmospheric moisture giving pink colouration • Acid attack leads to a carbonation front which could not be revealed by the indicator.
Infra-red Spectroscopy	• Based on infra-red spectroscopy	• Non-destructive testing • Possible to monitor formation of silica gel due to carbonation of calcium silicate hydrate.	• Accuracy depends on degree to which carbonation reaction has proceeded to the calcium silicate hydrate stage • Method is complex and expensive

Table 2.12 (contd) Summary of commonly used test methods for determining the carbonation depth of concrete

Test Method	Method	Advantages	Disadvantages
Thermal Analysis	Identifies and measures polymorphic forms of calcium carbonate . Apparatus used : • Differential Thermal Analysis • Thermogravimetry	• Distinguishes between different types of carbonate: calcite, vaterite and aragonite • Shows clearly the existence of a transitional zone, rather than a sharp interface • Averages CO_2 contents over the mass of a given sample	• Two interpretations can be obtained from similar DTA results on carbonated mortar • Requires use of expensive apparatus • Determination of $Ca(OH)_2$ may suffer from some systematic errors as a consequence of other thermal decomposition generating $Ca(OH)_2$, eg at lower temperatures the decomposition of calcium aluminate hydrate yields $Ca(OH)_2$ among other phases
X-Ray Diffraction	• Used as collaborative study to relate relative carbonate content with alkalinity interfaces indicated by phenolphthalein	• Well established qualitative method of evaluating products of carbonation • Distinguishes lines produced by calcite, vaterite and aragonite from each other and from those produced by other cement compounds • Ability to measure reduction of calcium hydroxide and increase of various forms of calcium carbonate	• Very detailed for use as routine test • Expensive apparatus
Microscopy	• Direct observation of pronounced double refraction in polarised light of calcium carbonate with optical microscope	• Distinct border between the unchanged hydrated phases of clinker and newly formed calcium carbonate is clearly seen in thin sections	• Requires thin sections for examination • Associated problems with production of sections

c = the amount of alkaline material available in unit volume of concrete to buffer carbon dioxide (kg/m^3).

hence:

$$x = k\sqrt{t} \tag{2.7}$$

where:

$$k = \sqrt{\frac{2Dr}{c}} \tag{2.8}$$

This equation is widely used due to its simplicity. However, it tends to ignore the following factors (Richardson 1988):

- The reduction of the rate of carbonation due to the reduction in permeability imposed by the deposition of $CaCO_3$ in the pore solution as time increases;
- The degree of saturation of the pores of concrete subjected to cyclic wetting and drying due to exposures in wet environments;
- The counter diffusion of the $Ca(OH)_2$ due to a concentration gradient from uncarbonated regions to carbonated regions;

- The tortuosity of the pores and the pore structure due to the influence of different cement groups. The assumption of linear variation of CO_2 concentration gradient may not be valid as this could hold true within the carbonated region but not where carbonation is actively taking place;
- CO_2 gas concentrations in the uncarbonated region are assumed to be zero and this may not be the case.

2.11.2 Predictive Models Based on Fickean Law

Concrete exposed to periodic rainfall may not show the same performance as dry concrete exposed indoors. An attempt was made by Bakker to simulate the effect of periodic wetting and drying on the depth of carbonation (Bakker 1993). The final form of the derived model is given in Equation 2.9 which is primarily based on applying Fick's law of diffusion twice, firstly to describe the drying of the carbonated concrete and secondly to describe the carbonation of dry concrete.

$$x_n = A\sqrt{td_1 + td_2 - \left(\frac{x_1}{B}\right)^2 + td_3 - \left(\frac{x_2}{B}\right)^2 + td_4 - \left(\frac{x_3}{B}\right)^2 + \ldots + td_n - \left(\frac{x_{n-1}}{B}\right)^2} \qquad (2.9)$$

Where,

$$A = \sqrt{\frac{2D_c}{a}(C_1 - C_2)} \qquad (2.10a)$$

$$B = \sqrt{\frac{2D_v}{b}(C_3 - C_4)} \qquad (2.10b)$$

where,

x_n = carbonation depth after the nth cycle

c = amount of alkaline substance in concrete, kg/m^3

D_c = the effective diffusion coefficient for CO_2 at a given moisture distribution in the pores, m^2/s

C_1-C_2 = concentration difference of CO_2 between air and the carbonation front, kg/m^3

t_{dn} = the length of the nth drying period, seconds

D_v = effective diffusion coefficient for water vapour at a given moisture distribution in the pores, m^2/s

C_3-C_4 = the moisture difference between air and the evaporation front, kg/m^3

b = the amount of water to evaporate from the concrete, kg/m^3.

The model assumes that the carbonation of concrete stops as long as the concrete is wet and for any carbonation to be initiated again that the concrete has to dry out (Bakker 1993). Moreover, the maximum depths of carbonation in all cases will be the depth at which the concrete has been dried out. When no wetting is involved, and as the concrete remains dry, the equation reduces to Equation 2.7. In the application of this model the CO_2 concentration at the carbonation front is assumed to be zero. Moreover, the carbonatable material considered is solely the CaO provided from the cements.

2.11.3 Empirical Models

Table 2.13 summarises selected empirical models that have been developed. In deducing these formulae the focus was aimed at relating the depth of carbonation to the w/c ratio and/or the 28 day compressive strength as these two parameters are generally considered to provide an adequate measure of the durability performance of concrete.

The empirical formulae derived by Kokubu and Nagataki (1989) based on 20 years of natural exposure were tested against data obtained from UK laboratory investigations. The equations tend to overestimate depths in outdoors exposures where the concrete is subjected to wetting and drying, indicating that the assumption that carbonation follows a $\sqrt{t}$ relationship in exposed concrete may not be valid.

A large number of empirically derived models incorporate constants which may only be applicable to the experimental data under consideration. An empirical model devised by Parrott (1994) takes into account the difference in performance of different cement groups. This is made through a factor introduced in the model that takes into account the available CaO that will contribute to buffering the carbonation reaction. In addition to this, the effect of the environmental conditions is taken into account through adjusting the n value to correspond with the change in relative humidity values. This model may have a more practical applicability as it considers some of the fundamental parameters involved in the carbonation process.

2.11.4 Computer Simulated Models

A number of computer based mathematical models have been used in an attempt to predict the carbonation of concrete. Neural networks such as those proposed by Buenfeld et al (1996), and Buenfeld and Hassanein (1998) have been considered. Buenfeld et al (1996) designed a network based on 39 input neurons covering 18 concrete variables and 11 exposure conditions. The network was trained with 6600 different depths of carbonation extracted from 68 research papers. However, the overall average error when tested was calculated as 27.5%. A probabilistic approach, using a deterministic model and advanced stoichiometric simulations, has also been proposed (Keršner et al, 1996). A Monte Carlo simulation was used and the statistical characteristics of basic parameters were estimated then utilised in a sensitivity and probabilistic analysis. The Latin Hypercube Sample was then used as a numerical simulation technique. The coefficient of variation for predicted depths of carbonation after 60 years was calculated as 23%. Keršner et al (1996) also found that ambient relative humidity had a deterministic effect on the variability of carbonation depths.

2.12 SUMMARY

The review of literature has confirmed that the cover concrete is the most important with regard to the ingress of deleterious agents. Unfortunately, cover concrete tends to be of the

Table 2.13 Common empirical formulae derived for predicting the depth of carbonation.

Equation and Author	Parameters
Nagataki et al, 1987	
$x_c = \sqrt{(9.63R + 30.8)\exp(-0.00441f)}\sqrt{t}$	R = replacement ratio f =compressive strength at end of curing t =time
Richardson, 1988	
$x = (n_1 n_2 n_3 n_4 n_5 k_{av})\sqrt{t}$	n_1=2, a carbonation front parameter n_2=0.6 for external exposure, otherwise unity n_3=concrete quality parameter n_4=0.3 for float-finished horizontal surfaces, otherwise unity n_5=CO_2 concentration parameter (e.g. 1.0 rural, 1.4 urban) k_{av}=correlation factor t = time
Dhir et al, 1989b	
$D_t = \left(\frac{t}{20}\right)^{\gamma}(22.8\log k - 6.9)$ $D_t = \left(\frac{t}{20}\right)^{\gamma}(82 - 34\log F_d)$	D_t= carbonation depth at 20°C, 50% RH and 4%CO_2 γ= 0.5 if w/c ≤0.6 0.4 if w/c > 0.6 t= exposure period k= intrinsic permeability (CAT) F_d= Figgs air permeation index t = time
Kokubu and Nagataki, 1989	
Outdoors $x = \left(10 - 1.6\sqrt{f'_{28}}\right)\sqrt{t}$ *Indoors* $x = \left(17 - 2.2\sqrt{f'_{28}}\right)\sqrt{t}$	x= depth of carbonation f'_{28}= 28 days compressive strength t = time
Ohga and Nagataki, 1989	
$x_c = \alpha\left(\beta - \sqrt{f'_{28}}\right)\sqrt{t}$ $x_c = \exp[\gamma(1 - \delta \times f'_{28})]\sqrt{t}$	α,β,γ,δ= experimental constants f'_{28}= 28 day compressive strength
Bob, 1990	
$x = \frac{150ckd}{f_c}t^{0.5}$	c = 1.0 for Romanian cement d = Influence of CO_2 f_c = Compressive strength k = 1 indoors, 0.7 outdoors sheltered, 0.5 outdoors, 0.3 for wet concrete t = time

Table 2.13(contd) Common empirical formulae derived for predicting the depth of carbonation.

Equation and Author	Parameters
Cementitious Slag Makers Association, 1995	
$x(t) = 7 \times \left(\frac{10w/c}{\sqrt{N_7}} - 0.175 \right) \sqrt{t} - 0.50$ $T = 5 + 0.003 \frac{N5 - 100}{10w/c} t$ $x(t) = \left(84.62 \frac{w/c}{\sqrt{N_7}} - 0.64 w/c - 1.63 \right) \sqrt{t} - 0.95$	x(t): carbonation depth, mm t : age of concrete in months N_T: standard compressive strength of the cement in kp/cm^2 after T days N_5: standard compressive strength of the cement in kp/cm^2 after 5 days N_7: standard compressive strength of the cement in kp/cm^2 after 7 days.
De Ceukelaire and Van Nieuwenburg, 1993	
$d = \sqrt{2D \frac{C_1}{C_0} t}$	d: depth of carbonation D: Diffusion Characteristics C_1: CO_2 Concentration C_0: Amount of CO_2 necessary for carbonation
Parrott, 1994a	
$d = aK^{0.4} t_i / c^{0.5}$ $m = 1.6 - 0.00115 \times r - 0.0001475 \times r^2$ $n = 0.02536 + 0.01785 \times r - 0.0001623 \times r^2$	K air permeability of the cover concrete, if K is unknown then $K=mK_{60}$ or m=1.10 if r< 60 K_{60} : permeability of concrete dried at 60% RH n : power exponent close to 0.5 for indoor exposure r : relative humidity C: CaO content in the hydrated cement matrix of the concrete cover a: coefficient assigned a value of 64 on the basis of the available published data
Loo et al, 1994	
$K = \alpha f_{28} C_0^b e^{cT} t^d {}_{WC} + \beta$	f_{28}: 28 day compressive strength C CO_2 concentration e ambient temperature t water curing duration
Hobbs, 1994	
$(C_1)_{PC} = (C_2 + 0.56\rho)_{PFA}$ $d_c = ([A(W/C + 0.2\rho)] - B) \times t^{\frac{1}{2}}$ $(W_1/C_1)_{PC} = [(W_2)/(C_2 + 0.3)]_{PFA}$	where ρ=pfa content

poorest quality when compared to a concrete section such that design, materials execution and curing are all vital factors in ensuring that the durability of concrete is sufficient to withstand the effects of the surrounding environment.

The move forward to produce standards based on performance has encouraged research into a number of areas including new and existing test methods for determining concrete performance. One such test for carbonation is already in draft form although trials have shown precision to be poor. The test was, however, identified as having the potential for use as a specification test.

A review of the carbonation mechanism showed that although it is generally termed a diffusion controlled reaction, the rate of diffusion is controlled by both the physical and chemical nature of the concrete. Pore size, distribution and interconnectivity will physically prevent the ingress of the CO_2 gas, while the alkaline nature of the pore fluids will reduce the neutralisation effect of the CO_2 on dissolving.

Micro and macro climates will affect the carbonation of concrete which is heavily dependent on relative humidity and temperature. The level of pore saturation also affects the progress of carbonation, with higher apparent levels of pore moisture reducing the effects of carbonation. Concrete containing pozzolanic materials such as PFA, MK and CSF carbonate at a greater rate than PC concrete. However this depends on the length of curing and degree of exposure of the concrete to moisture during the carbonation period.

A number of theoretical and empirical predictive models have been assessed and advantages and disadvantages of each promoted. The theoretical models are based on a number of assumptions whereas the majority of the empirical formulae are only suitable under a certain set of criteria.

CHAPTER 3

EXPERIMENTAL PROGRAMME, MATERIAL PROPERTIES AND TEST PROCEDURES

3.1 INTRODUCTION

The main objectives of the research study were to examine the technical and practical feasibility of developing a real time simulated natural carbonation test to predict the long term carbonation of common cement types used in BS EN 197-1. This was mainly because the number of cement types now available within the UK and the rest of Europe has increased rapidly over the last decade and the long term performance of concrete structures built with these new cements is relatively unknown. Hence, the development of a relatively quick performance based test will provide a much needed tool to assess the suitability of individual concrete structures for use in different environments.

The research also assessed the effect of using relatively finer cements, such as metakaolin and condensed silica fume, and fine inert fillers to reduce permeation and increase the durability of concrete in carbonating environments.

With the move towards performance based specifications for the new generation of Eurocodes, the development of a simulated natural carbonation test was undertaken. Problem areas were identified from an initial Round Robin Series carried out throughout Europe and the test method enhanced in these areas respectively. The idea of benchmarking the performance of concrete of unknown performance against a concrete of known performance was investigated to assess the feasibility of promoting a reference mix within the UK against which the performance of other cement types may be assessed.

Published long term data was compared to the simulated natural carbonation test data and a predictive analysis carried out to evaluate the long term carbonation performance of the various cement types.

3.2 EXPERIMENTAL PROGRAMME

The experimental programme for the research study is shown in Figure 3.1.

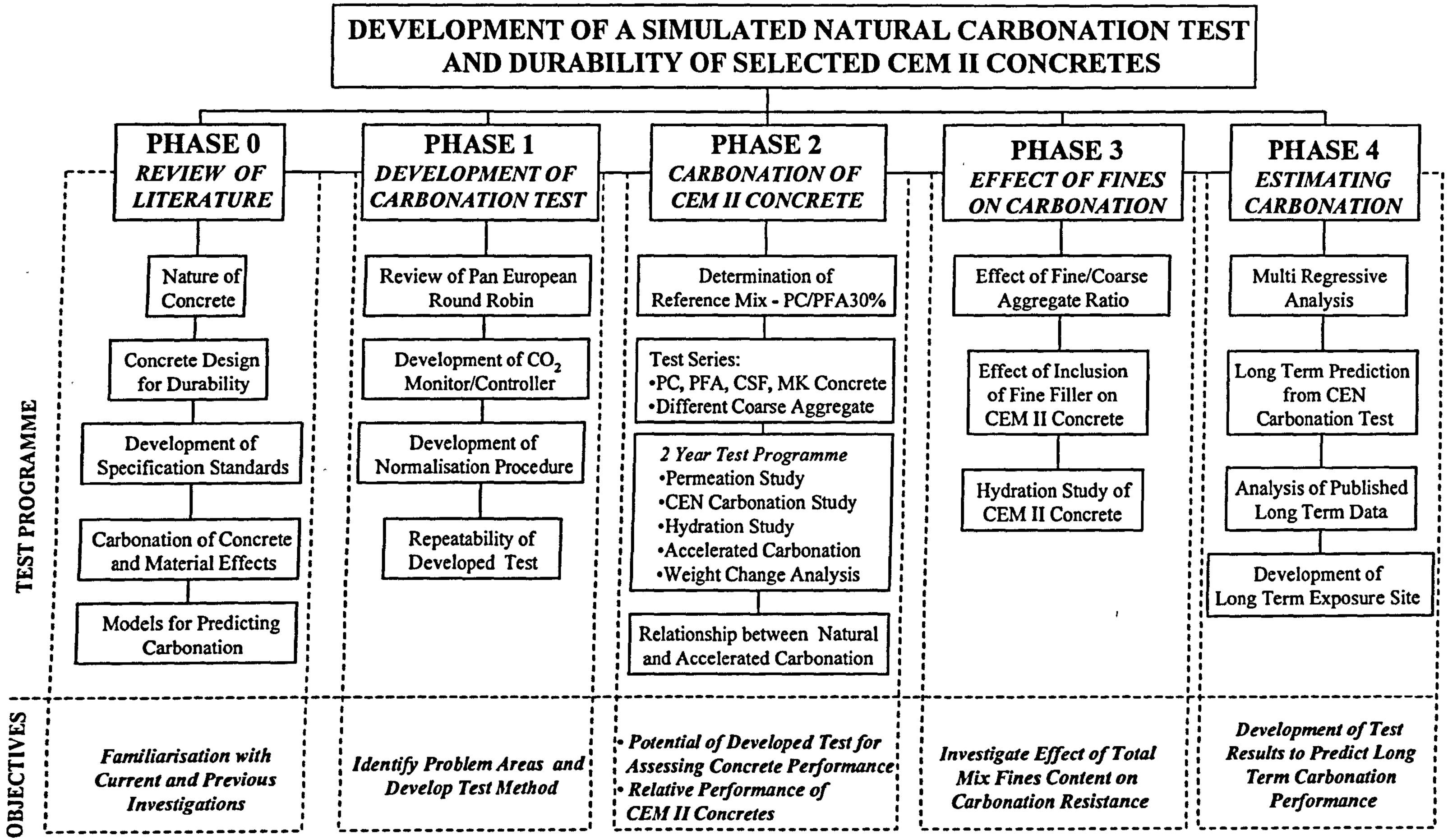


Figure 3.1 Experimental Programme

3.3 MATERIALS TESTED

3.3.1 Portland Cement

A single source Portland cement complying with BS 12: 1991 and BS ENV 197 Part 1 - Grade 42.5N was used. The cement was stored in air tight containers to prevent deterioration with time. The chemical and physical details of the cements are shown in Table 3.1 and Figure 3.2a.

3.3.2 Pulverized-Fuel Ash (PFA)

A bulk single source PFA complying with BS EN450/BS 3892: Part 1: 1997 was used throughout the research. The chemical and physical details are also listed in Table 3.1 and Figure 3.2a.

3.3.3 Metakaolin (MK)

A single source supply of the ECC product MetaStar 501 was used and the material was transferred to water and air tight plastic bags on delivery. The material had the British Board of Agrément Certificate (number 98/3540) and the properties are given in Table 3.1 and Figure 3.2b.

3.3.4 Condensed Silica Fume (CSF)

The CSF used throughout the project was 1:1 slurry of CSF and water, compliant with the British Board of Agrément (certificate number 85/1568). The water content of the concrete mix was adjusted accordingly during the trial mixing and design stage. The chemical and physical properties are also given in Table 3.1 and Figure 3.2c.

3.3.5 Coarse Aggregate

Four sources of coarse aggregates with the grading meeting the requirements of BS 882:1992 were used. These include a bulk supply of local natural gravel in two size fractions 5-10mm and 10-20mm and an alternative Thames Valley Gravel in two single sizes of 10mm and 20mm. Two sources of crushed rock were also considered in the research programme. A crushed Aberdeenshire Granite and a crushed Yorkshire Limestone were used in two single sizes of 10mm and 20mm.

The chemical and physical characteristics of coarse aggregates used are given in Tables 3.2 and 3.3. The particle size distribution of the coarse aggregates is shown plotted in Figures 3.3 and 3.4 All coarse aggregates were washed prior to use in concrete production.

Table 3.1 Chemical and selected physical characteristics of cements used in the project.

Property	PC	PFA	MK	CSF
Chemical Composition, %				
SiO_2	21.4	49.9	55.0	92.0
Al_2O_3	4.6	26.1	40.0	1.0
Fe_2O_3	2.3	9.3	0.6	1.0
CaO	66.2	1.5	0.1	0.3
MgO	1.1	1.4	0.4	0.6
SO_3	2.1	0.8	2.4	0.3
K_2O	0.2	3.6	0.1	0.8
Na_2O	0.6	1.7	nd	0.3
Ti_2O	nd	1.0	nd	nd
MnO	nd	nd	nd	nd
Free Lime	1.2	nd	nd	nd
L.O.I.	0.7	4.3	-	-
Insoluble Residue	0.2	nd	nd	nd
Bogue Compound[1], %				
C_3S	66.6	-	-	-
C_2S	11.5	-	-	-
C_3A	8.3	-	-	-
C_4AF	7.0	-	-	-
Mineralogy, %				
Quartz	-	2.4	-	nd
Mullite	-	2.5	-	nd
Magnetite	-	0.6	-	nd
Hematite	-	3.1	-	nd
Glass	-	88.0	-	99.9
Compressive Strength[2] EN 196-1, N/mm²				
2 days	26.1	-	-	-
7 days	47.5	-	-	-
28 days	61.5	-	-	-
Specific gravity[2]	3.15	2.20	2.25	2.25

[1] Calculated by author using Bogue Equations.

[2] Data from manufacturer.

nd = none detected

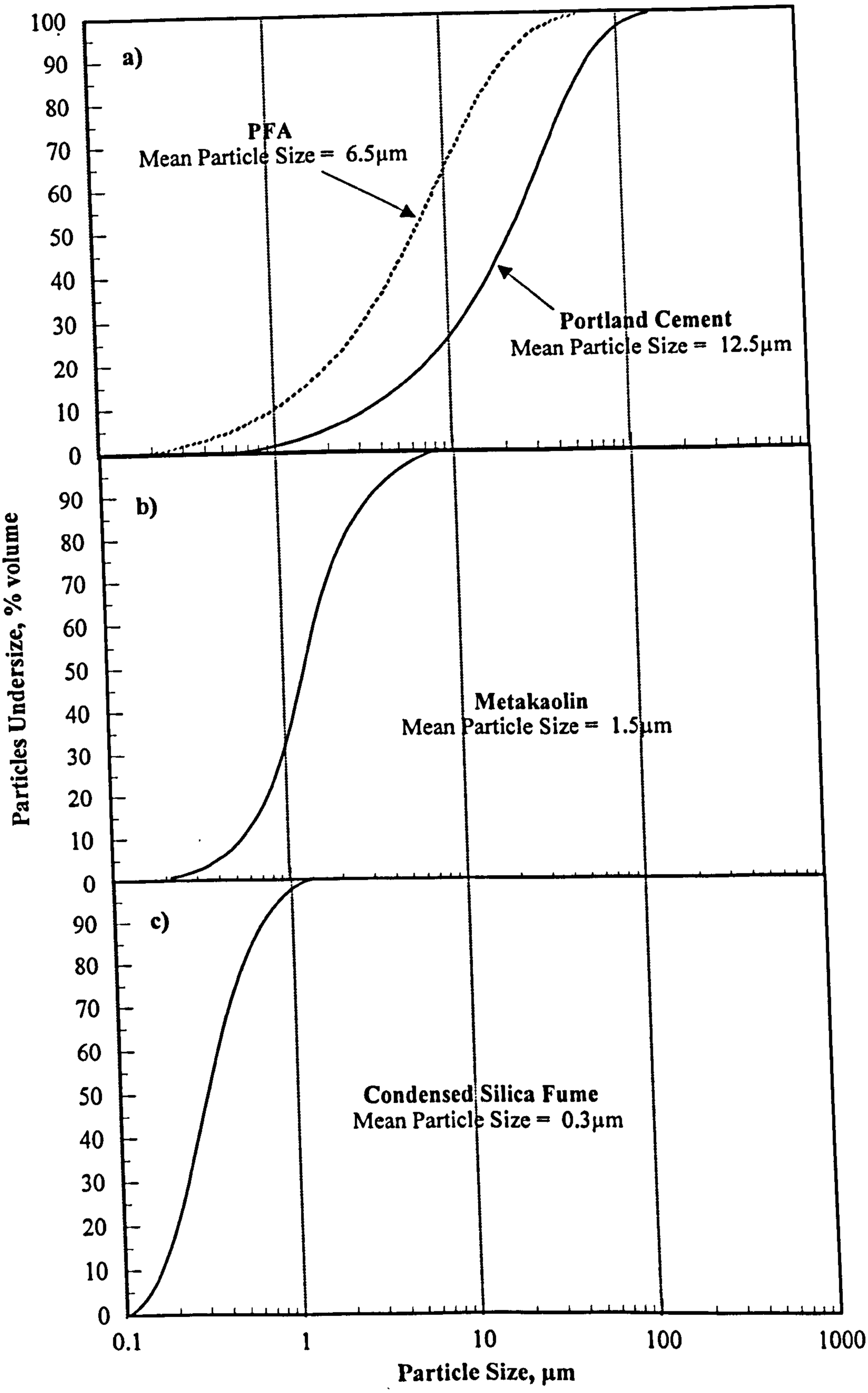


Figure 3.2 Particle size distribution of cements used in current study determined using the Malvern Laser Particle Sizer.

Table 3.2 Chemical characteristics of limestone filler, fine and coarse aggregates.

Oxide	Bulk Oxide Content, %									
	Filler	Fine Aggregate	Coarse Aggregates							
	Limestone [1]	Sand	Natural Fife Gravel		Thames Valley Gravel		Crushed Granite		Crushed Limestone	
			5-10mm	10-20mm	10mm	20mm	10mm	20mm	10mm	20mm
CaO	55.5	2.2	2.1	2.2	1.6	1.8	1.3	1.2	48.9	60.0
SiO_2	nd	70.1	66.9	66.2	82.9	84.8	68.5	69.7	nd	nd
Al_2O_3	0.1	10.5	11.7	12.3	4.5	7.4	14.3	14.0	0.4	0.3
Fe_2O_3	0.1	5.8	5.7	5.9	0.8	0.5	2.5	2.1	6.4	0.1
MgO	0.1	3.1	3.2	2.7	0.3	0.1	0.4	0.6	1.1	1.3
K_2O	nd	1.8	2.6	2.6	0.2	0.1	4.8	4.9	0.1	0.1
Na_2O	nd	2.8	2.4	3.1	1.0	0.8	2.8	3.3	nd	0.1
TiO_2	nd	0.7	0.8	0.9	0.8	0.2	0.2	0.3	nd	nd
MnO	nd	0.1	0.1	0.1	0.2	0.1	nd	0.1	nd	nd
P_2O_5	nd	0.2	0.3	0.3	nd	nd	0.1	0.1	nd	nd
L.O.I.	43.6	2.1	2.7	2.6	5.2	1.6	1.4	1.5	41.7	37.2

nd = none detected

[1] Calcium present as 99.1% $CaCO_3$

Table 3.3 Physical characteristics of fine and coarse aggregates.

	Particle Shape [1]	Surface Texture [1]	Elongation Index[2]	Flakiness Index[3]	Absorption[1] at 24 hours, %	Relative Density[4]	Loose Bulk Density[1], kg/m³
Filler	-	-	-	-		2.65	
Sand	-	-	-	-	0.8	2.69	1620
Natural Fife Gravel							
5-10mm	Rounded	Smooth	14	11	1.7	2.56	1535
10-20mm	Rounded	Smooth	15	12	1.5	2.56	1420
Thames Valley Gravel							
10mm	Rounded	Smooth	15	12	3.0	2.50	1365
20mm	Rounded	Smooth	17	14	1.0	2.56	1480
Crushed Granite							
10mm	Angular	Coarse/ Crystalline	19	14	0.8	2.62	1300
20mm	Angular		20	14	0.4	2.62	1355
Crushed Limestone							
10mm	Angular/ Irregular	Rough	21	16	0.6	2.61	1360
20mm		Rough	22	16	0.6	2.61	1385

[1] To BS 812: Part 1: 1990

[2] To BS 812: Part 105.1:1990

[3] To BS 812: Part 105.2:1990

3.3.6 Fine Aggregate

Fine aggregate used was a natural sand which complying with Zone M of BS 882:1992. The particle size distribution of the sand is shown plotted in Figure 3.5.

3.3.7 Limestone Filler

The filler used was a commercial calcium carbonate crushed limestone. The chemical characteristics are given in Table 3.2 and the physical characteristics shown in Table 3.3 and Figure 3.5.

3.3.8 Water Reducing Admixture

A normal range water reducing admixture, complying with BS 5075:Part 1 1985 was used in to achieve the desired workability of slump class S2 in BS EN 206-1, where required. The admixture was suitable for use with all cement types in BS EN 197-1. The main characteristics of the admixture are given in Table 3.4.

3.3.9 Water

Mains water with a pH of 5.0 ± 0.5. was used throughout the concrete production procedures.

3.4 CONCRETE MIX PROPORTIONS

Four series of concrete mixes were cast. Within each series, three mixes were cast for each cement combination as below:

- One primary mix, judged to give a 28 day compressive strength of 37N/mm^2
- Two secondary mixes, one with +25kg/m^3 and one with -25kg/m^3 of the total cement content of the primary mix.

This allowed the normalisation of mix proportions to achieve an exact 28 day strength of 37N/mm^2 giving comparison of performance at equal grade. Further details of this procedure are described in Chapter 4. All concrete mixes were proportioned following the steps given in the BRE method (Techeynne et al, 1997), ensuring workability was consistent and complying with slump class S2 (60 to 90mm) in BS EN 206-1.

3.4.1 Series 1 Different Cement Types: CEM I and CEM II (Main Test Series)

A series of eight cement combinations were selectively used in Series 1. The main aim of this work was to compare the effects of unfamiliar cement types on concrete performance in a carbonating environment. The details of the mix proportions are given in Table 3.5.

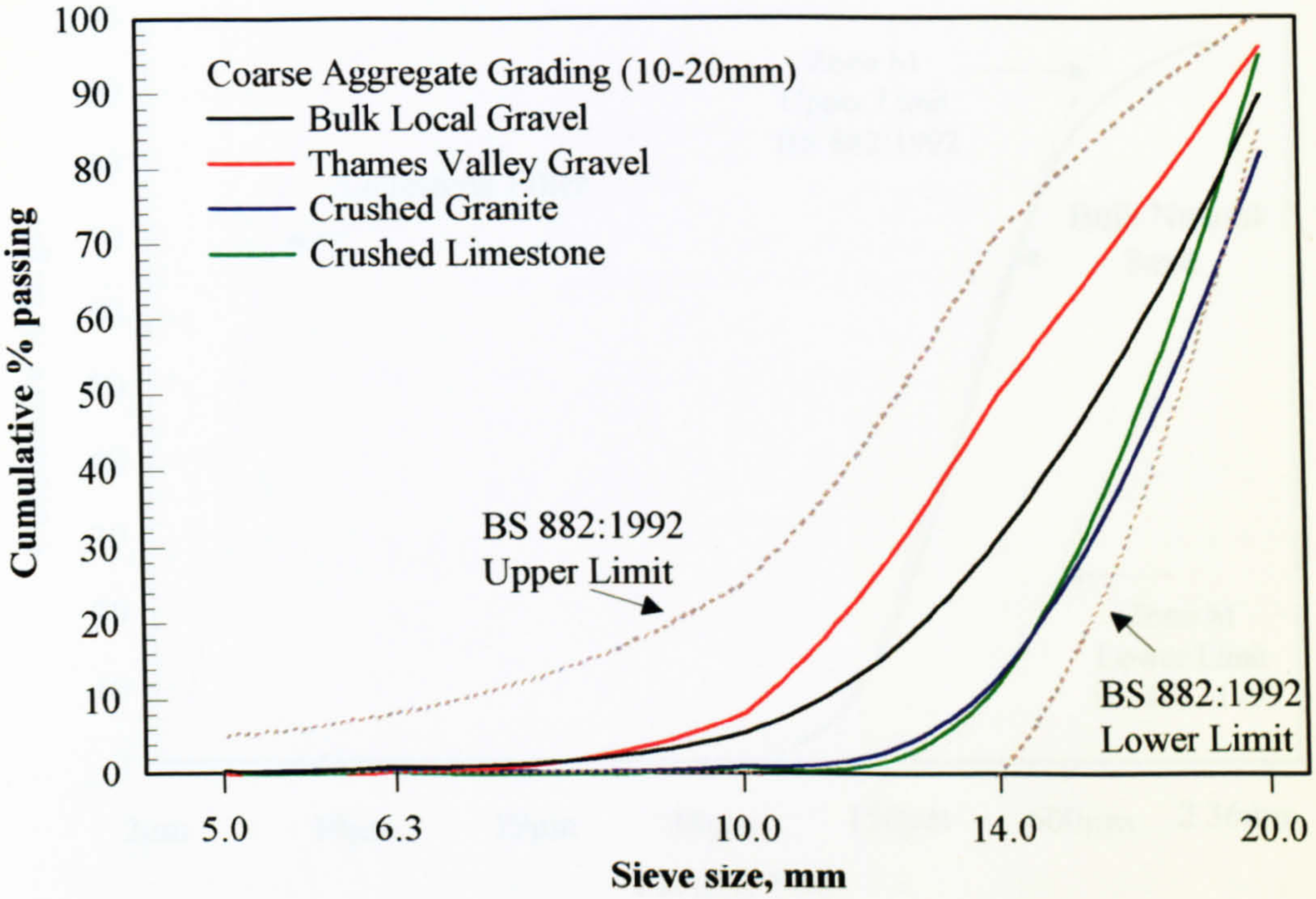


Figure 3.3 Particle size distribution of 10-20mm coarse aggregates used on project.

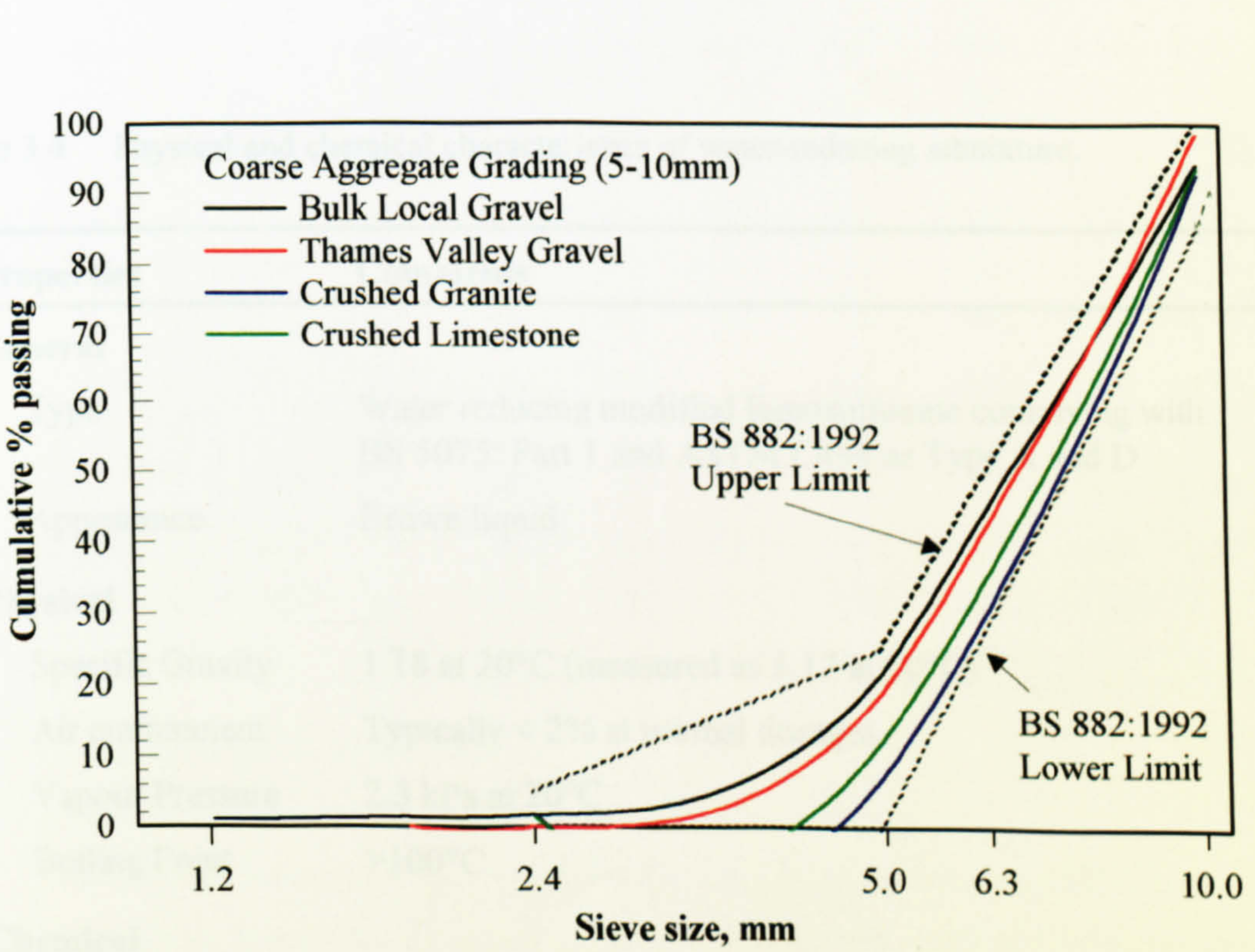


Figure 3.4 Particle size distribution of 5-10mm coarse aggregates used on project.

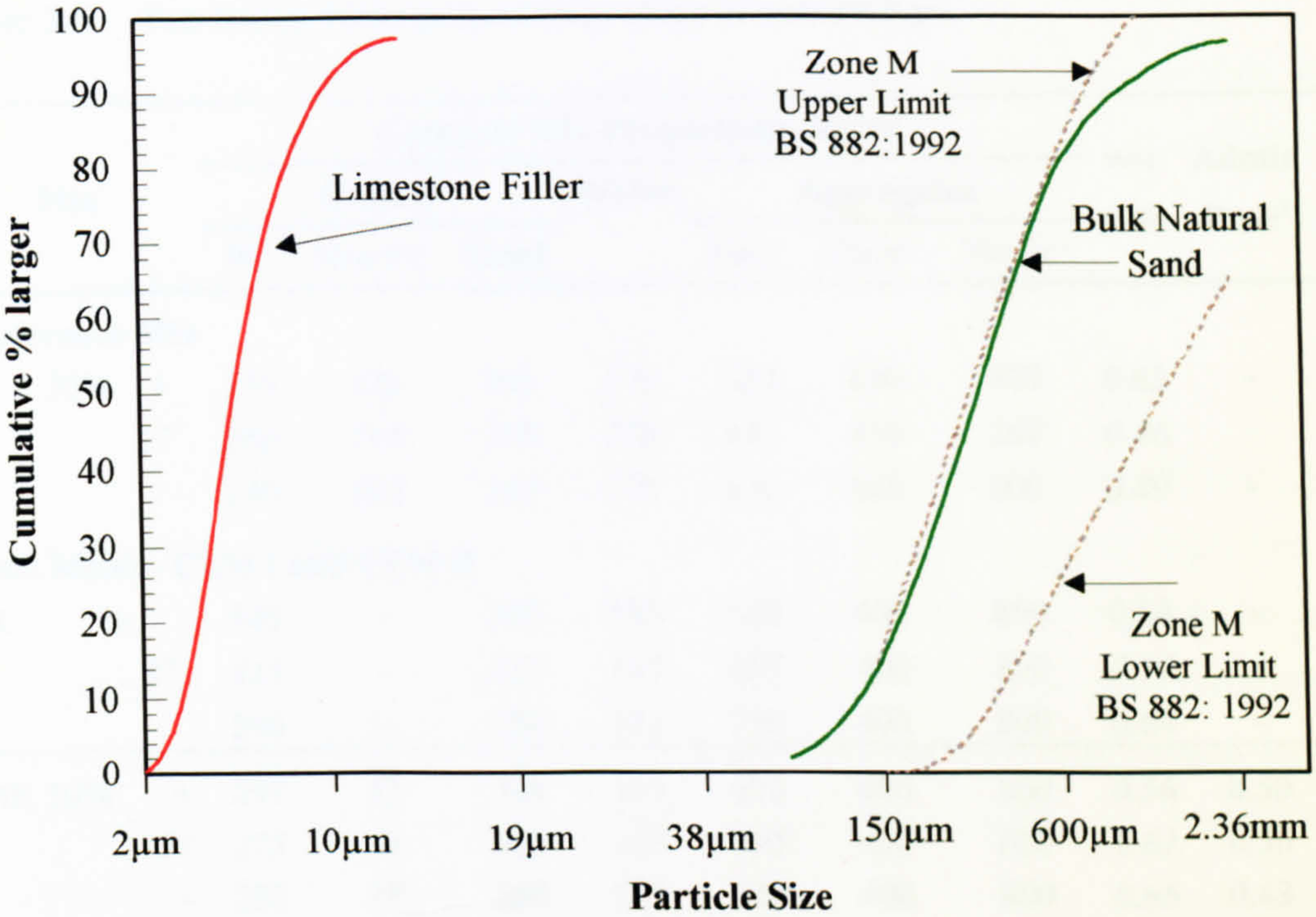


Figure 3.5 Particle size distribution of limestone filler and bulk natural sand, used as fine aggregate.

Table 3.4 Physical and chemical characteristics of water-reducing admixture.

Properties	Comments
General	
Type	Water reducing modified lignosulfonate complying with BS 5075: Part 1 and ASTM C494 as Type A and D
Appearance	Brown liquid
Physical	
Specific Gravity	1.18 at 20°C (measured as 1.17 at 20°C)
Air entrainment	Typically < 2% at normal dosages
Vapour Pressure	2.3 kPa at 20°C
Boiling Point	>100°C
Chemical	
pH (concentrate)	8.0 (measured as 8.4)
Chloride content	Nil to BS 5075
Alkali content	Typically < 5.0g Na_2O equivalent per litre

Table 3.5 Test Series 1 mix proportions, effect of cement type.

Mix*	Concrete Mix Proportions, kg/m³							w/c ratio	Admix Dose[2]	Slump, mm
	Cement			Water	Aggregates					
	PC	Non PC	Total		Sand	10mm[1]	20mm[1]			
Reference Mix										
PFA 30% +	275	120	395	170	620	400	800	0.43	-	70
37	*260*	*110*	*370*	*170*	*645*	*400*	*800*	*0.46*	-	*75*
-	240	105	345	170	670	400	800	0.49	-	75
Test Mixes - CEM I and CEM II										
PC +	340	-	340	185	660	400	800	0.54	-	75
37	*315*	-	*315*	*185*	*685*	*400*	*800*	*0.59*	-	*80*
-	290	-	290	185	710	400	800	0.64	-	80
MK 10% +	297	33	330	185	670	400	800	0.56	0.50	75
37	*275*	*30*	*305*	*185*	*695*	*400*	*800*	*0.61*	*0.50*	*75*
-	252	28	280	185	720	400	800	0.66	0.43	75
MK 15% +	272	48	320	185	680	400	800	0.58	0.50	80
37	*250*	*45*	*295*	*185*	*705*	*400*	*800*	*0.63*	*0.42*	*75*
-	230	40	270	185	730	400	800	0.69	0.37	75
MK 20% +	252	63	315	185	685	400	800	0.59	0.50	70
37	*232*	*58*	*290*	*185*	*710*	*400*	*800*	*0.64*	*0.42*	*70*
-	212	53	265	185	735	400	800	0.70	0.40	80
CSF 10% +	279	31	310	185	690	400	800	0.60	0.30	75
37	*256*	*29*	*285*	*185*	*715*	*400*	*800*	*0.65*	*0.30*	*75*
-	234	26	260	185	740	400	800	0.71	0.30	80
CSF 15% +	280	50	330	185	670	400	800	0.56	0.30	80
37	*259*	*46*	*305*	*185*	*695*	*400*	*800*	*0.61*	*0.30*	*80*
-	238	42	280	185	720	400	800	0.66	0.30	75
CSF 20% +	270	70	340	185	660	400	800	0.54	0.35	75
37	*250*	*65*	*315*	*185*	*685*	*400*	*800*	*0.59*	*0.35*	*75*
-	230	60	290	185	710	400	800	0.64	0.35	75

[1] Coarse aggregate is natural gravel

[2] Admixture dosage in litres/100kg of total cement

* Mixes in italics are the primary mixes having a target 28 day strength of 37N/mm². Mixes with + and- symbols are secondary mixes having a total cement content of +25kg/m³ and - 25kg/m³ of the primary mix.

3.4.2 Series 2: Different Aggregate Types

Coarse aggregate obtained from four different sources were used to examine their influence on carbonation resistance of concrete. These included two sources of gravel (one local and one from Thames Valley) and two sources of crushed rock, namely Aberdeenshire granite and Yorkshire limestone. The mix constituent proportions for this test series are given in Table 3.6.

3.4.3 Series 3: Adjusted Fine/Coarse Aggregate Ratio

Concretes with adjusted fine/coarse aggregate ratios were also tested to examine the influence of fine aggregate content on carbonation resistance. The fine/coarse aggregate ratio as recommended in the BRE mix design method (Techeynne et al, 1997) was adjusted by ±10% to examine the effects of the fine/coarse aggregate ratio on the carbonation resistance. The increase in fine/coarse aggregate ratio was an attempt to increase the total mass of fine particles less than 125μm and to observe the effect on carbonation resistance. The concrete mix proportions are shown in Table 3.6.

3.4.4 Series 4: Adjusted Fines (<125μm) Contents

Concrete mixes developed from Series 1 were slightly adjusted by the partial replacement of sand with a limestone filler. This increased the total fines (defined as particles less than 125μm) but did not affect the fine/coarse aggregate ratio . The workability was kept constant by means of the low range water reducing admixture where required. These mixes are detailed in Table 3.7.

3.5 PREPARATION OF TEST SPECIMENS

3.5.1 Mixing of Concrete

Mixing of concrete was carried out in a horizontal pan mixer of 0.04m³ capacity. The fine and coarse aggregates were dry mixed for 30 seconds and then for a further 30 seconds with half the water added. After allowing approximately 8 minutes for aggregate water absorption, the cement and any secondary cement and/or filler were added and mixed for 1 minute. The remaining water (and admixture where required) was then added and mixed for a further 3 minutes. To ensure homogeneity, the concrete was hand mixed.

3.5.2 Determination of Concrete Plastic Density

The plastic density of the fresh concrete was measured in accordance with BS 1881: Part 107: 1983. A sample of the fresh concrete was placed into a water tight container of known volume and compacted in six equal layers. The mass of the concrete was measured and the plastic density of the fresh mix calculated.

Table 3.6 Test Series 2 and Test Series 3 mixes.

Mix	Concrete Mix Proportions, kg/m³							w/c ratio	Admix Dose[1]	Slump, mm
	Cement			Water	Aggregates					
	PC	Non PC	Total		Sand	10mm	20mm			
Test Series 2 Mixes - Alternative Coarse Aggregate Sources										
Thames Valley Gravel										
PFA 30% +	275	120	395	170	620	400	800	0.43	-	70
37	*260*	*110*	*370*	*170*	*645*	*400*	*800*	*0.46*	-	*70*
-	240	105	345	170	670	400	800	0.49	-	75
Crushed Aberdeenshire Granite										
PFA 30% +	262	113	375	190	620	400	800	0.51	-	80
37	*245*	*105*	*350*	*190*	*645*	*400*	*800*	*0.54*	-	*75*
-	228	97	325	190	670	400	800	0.58	-	75
PFA 30% +	275	120	395	170	620	400	800	0.43	0.32	75
37	*260*	*110*	*370*	*170*	*645*	*400*	*800*	*0.46*	*0.33*	*80*
-	240	105	345	170	670	400	800	0.49	0.33	80
Crushed Yorkshire Limestone										
PFA 30% +	259	111	370	190	625	400	800	0.51	-	75
37	*242*	*103*	*345*	*190*	*650*	*400*	*800*	*0.55*	-	*80*
-	224	96	320	190	675	400	800	0.59	-	75
PFA 30% +	275	120	395	170	620	400	800	0.43	0.31	80
37	*260*	*110*	*370*	*170*	*645*	*400*	*800*	*0.46*	*0.30*	*80*
-	240	105	345	170	670	400	800	0.49	0.31	75
Test Series 3 Mixes - Adjusted Fine/Coarse Aggregate Ratio[2]										
+10% Fine/Coarse Aggregate Ratio										
PFA 30% +	275	120	395	170	815	340	680	0.43	0.30	70
37	*260*	*110*	*370*	*170*	*830*	*340*	*680*	*0.46*	*0.35*	*70*
-	240	105	345	170	855	340	680	0.49	0.35	75
PC +	340	-	340	185	815	350	695	0.54	0.30	75
37	*315*	-	*315*	*185*	*840*	*350*	*695*	*0.59*	*0.30*	*80*
-	290	-	290	185	865	350	695	0.64	0.30	75
-10% Fine/Coarse Aggregate Ratio										
PFA 30% +	275	120	395	170	440	460	920	0.43	-	85
37	*260*	*110*	*370*	*170*	465	460	920	*0.46*	-	*85*
-	240	105	345	170	490	460	920	0.49	-	75
PC +	340	-	340	185	450	470	940	0.54	-	85
37	*315*	-	*315*	*185*	*475*	*470*	*940*	*0.59*	-	*85*
-	290	-	290	185	500	470	940	0.64	-	75

[1] Admixture dosage in litres/100kg of total cement

[2] Coarse aggregate is natural gravel.

Table 3.7 Series 4 mixes - limestone filled mixes.

Mix	% LS[1] Filler	Concrete Mix Proportions, kg/m³								w/c ratio	Admix Dose[4]
		Cement				Aggregates					
		PC	Non PC	Total	Water	LS[2]	Sand	10mm[3]	20mm[3]		
PC/PFA 30%	*0*	265	110	375	170	0	640	400	800	0.46	-
	5	265	110	375	170	30	610	400	800	0.46	-
	10	265	110	375	170	65	575	400	800	0.46	0.10
	15	265	110	375	170	95	545	400	800	0.46	0.12
	20	265	110	375	170	130	510	400	800	0.46	0.15
PC	*0*	300	-	300	185	0	700	400	800	0.59	-
	5	300	-	300	185	35	665	400	800	0.59	-
	10	300	-	300	185	70	630	400	800	0.59	0.13
	15	300	-	300	185	105	595	400	800	0.59	0.23
	20	300	-	300	185	140	560	400	800	0.59	0.24
MK 10%	*0*	280	35	315	185	0	685	400	800	0.61	0.55
	5	280	35	315	185	35	650	400	800	0.61	0.56
	10	280	35	315	185	70	615	400	800	0.61	0.57
	15	280	35	315	185	105	580	400	800	0.61	0.59
	20	280	35	315	185	135	550	400	800	0.61	0.59
MK 15%	*0*	240	45	285	185	0	715	400	800	0.63	0.62
	5	240	45	285	185	35	680	400	800	0.63	0.62
	10	240	45	285	185	70	645	400	800	0.63	0.63
	15	240	45	285	185	105	610	400	800	0.63	0.64
	20	240	45	285	185	145	570	400	800	0.63	0.65
MK 20%	*0*	225	55	280	185	0	720	400	800	0.64	0.63
	5	225	55	280	185	35	685	400	800	0.64	0.64
	10	225	55	280	185	70	650	400	800	0.64	0.66
	15	225	55	280	185	110	610	400	800	0.64	0.67
	20	225	55	280	185	145	575	400	800	0.64	0.67
CSF 10%	*0*	250	30	280	185	0	720	400	800	0.66	0.60
	5	250	30	280	185	35	685	400	800	0.66	0.61
	10	250	30	280	185	70	650	400	800	0.66	0.62
	15	250	30	280	185	105	610	400	800	0.66	0.63
	20	250	30	280	185	145	575	400	800	0.66	0.65
CSF 15%	*0*	240	45	285	185	0	715	400	800	0.64	0.61
	5	240	45	285	185	35	680	400	800	0.64	0.61
	10	240	45	285	185	70	645	400	800	0.64	0.62
	15	240	45	285	185	110	610	400	800	0.64	0.63
	20	240	45	285	185	145	570	400	800	0.64	0.64
CSF 20%	*0*	230	60	290	185	0	710	400	800	0.63	0.63
	5	230	60	290	185	35	675	400	800	0.63	0.64
	10	230	60	290	185	70	640	400	800	0.63	0.65
	15	230	60	290	185	105	605	400	800	0.63	0.66
	20	230	60	290	185	145	585	400	800	0.63	0.67

[1] Percentage replacement by weight of fine aggregate [2] Limestone filler

[3] Coarse aggregate is natural gravel [4] Admixture dosage in litres/100kg of total cement

3.5.3 Measurement of Slump

The workability of the fresh concrete was measured by means of a slump test performed in accordance with BS 1881: Part 102: 1983. A sample of concrete is placed in a 300mm high steel mould in three equal layers, each layer being tamped25 times using a steel rod. Each layer is tamped to its full depth and just into the layer below. After tamping the top layer, the excess concrete is struck off and the mould removed gently within 5 to 10 seconds. Immediately after the mould has been removed the slump is measured to the nearest 5mm using a steel rule to determine the difference between the height of the mould and the highest point of the specimen being tested.

3.5.4 Casting of Concrete

Casting of specimens was in accordance with BS 1881: Part 108 1983. Immediately after casting, the moulds were placed under damp hessian for 24 hours before being transferred to the appropriate curing regime.

3.6 TEST METHODOLOGIES

3.6.1 Testing for Compressive Strength

Compressive strength tests were carried out in accordance with BS 1881:Part 116 1983 using three 100mm cubes at each test age. The compressive strength was expressed as the arithmetic average of the three readings.

3.6.2 Permeation Tests

3.6.2.1 Initial surface absorption test (ISAT)

ISAT tests were carried out in accordance with the method proposed by Byars (1992). This method was a refinement of the method developed by Dhir et al (1987) which was based on the British Standard BS 1881: Part 5 1970. 150mm cube specimens were tested at each age. Pre-conditioning of the specimens involved oven drying at 105°C to achieve constant weight change over a 24 hour period.

Ensuring that the tap was closed, the reservoir was filled to a head of 200mm. With the time being recorded by stopwatch, the tap was opened and water allowed to flow into the cap and through the outlet into the capillary tube to remove all air from the system. Any excess air in the system was removed by allowing the capillary tube to overflow. Ensuring that reservoir head was maintained at 200mm, the test was left to run.

Readings were taken at 10, 30, 60 and 120 minute intervals. Prior to each reading interval, the tap on the inlet tube was closed and the distance that the meniscus moved in millimetres within the capillary tube in a 60 second period was recorded as *d*. After the 60 second period the tap was opened and the test allowed to continue until the next reading interval.

The Initial Surface Absorption (ISA) values are calculated in ml/m^{2}s as:

$$ISA = F_c\, d \qquad (3.1)$$

where F_c = calibration factor

d = distance moved by meniscus in 60 seconds, mm

The results for the Initial Surface Absorption Test were plotted on a log ISA versus log time graph. For the purposes of the project, the ISA results were expressed as ISA-10, that is the ISA measured at 10 minutes. The ISA-10 was chosen as it is this value which is commonly measured insitu. The ISAT apparatus is illustrated in Figure 3.6.

3.6.2.2 Water vapour diffusivity

Water Vapour Diffusivity was carried out using a single cell transmission test developed at the University of Dundee (Dhir et al, 1989c). A 100mm core was extracted from a 150mm cube at the relevant test ages and the outer 25mm sliced using a diamond saw. A 25mm thick slice was also taken from the inner core of the concrete to evaluate the difference between the outer surface and inner properties of the concrete.

The specimens were oven dried at 105°C until constant weight was achieved. The specimens were then sealed into a stainless steel test cup, details of which are shown in Figure 3.7(a). The test cup was filled with 25mm± 2mm distilled water to ensure an upstream relative humidity of 100% and the specimen sealed into the cup by means of a rubber gasket in the support flange of the cup. The cup and specimen were weighed and placed in the test cabinet, Figure 3.7(b).

The temperature was maintained at 25°C by means of an electric heater and Peltier effect cooling pump in the range 10 to 30°C ± 0.1°C. The relative humidity was maintained at 0-2% by means of a silica gel desiccant.

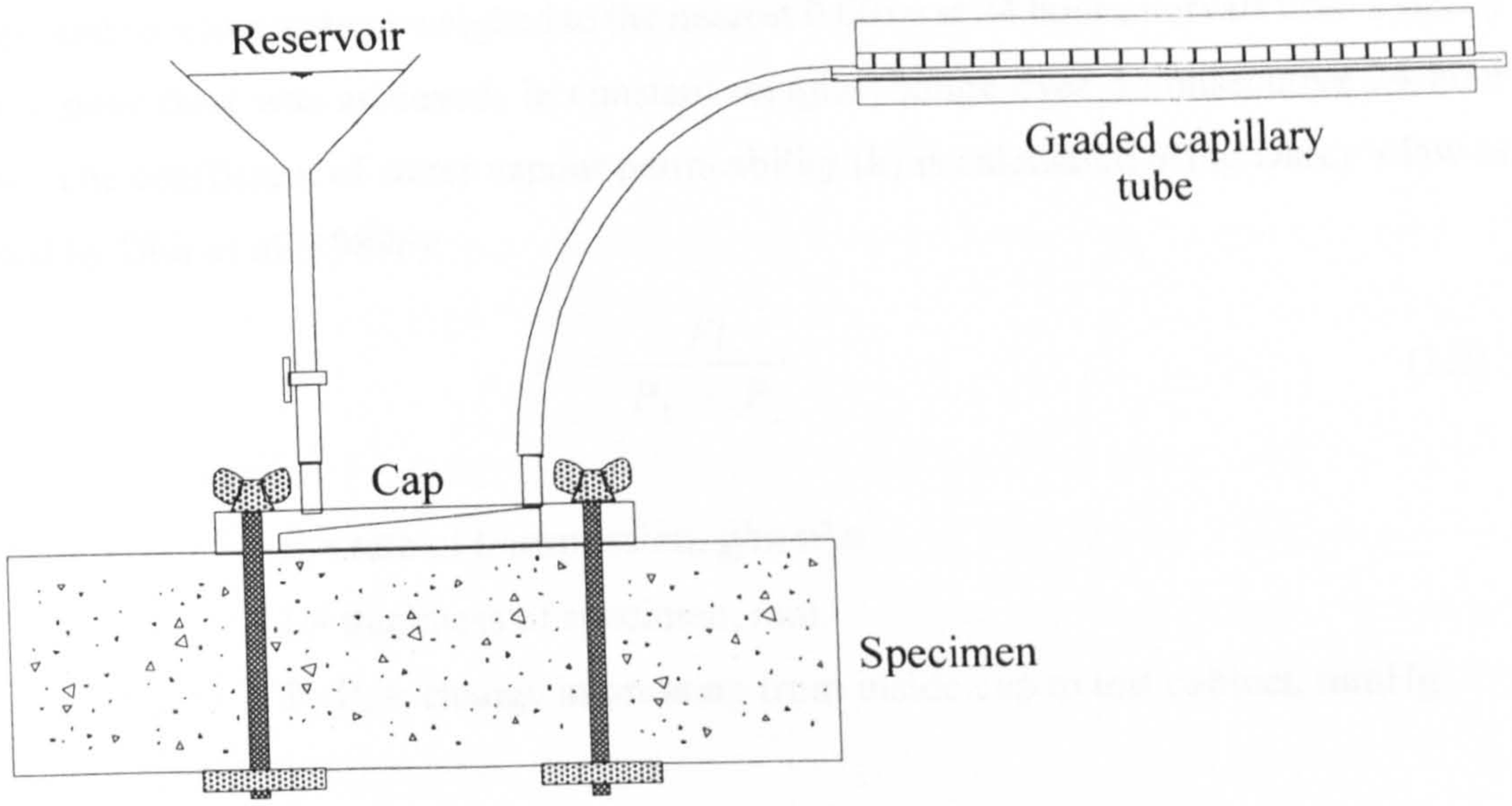
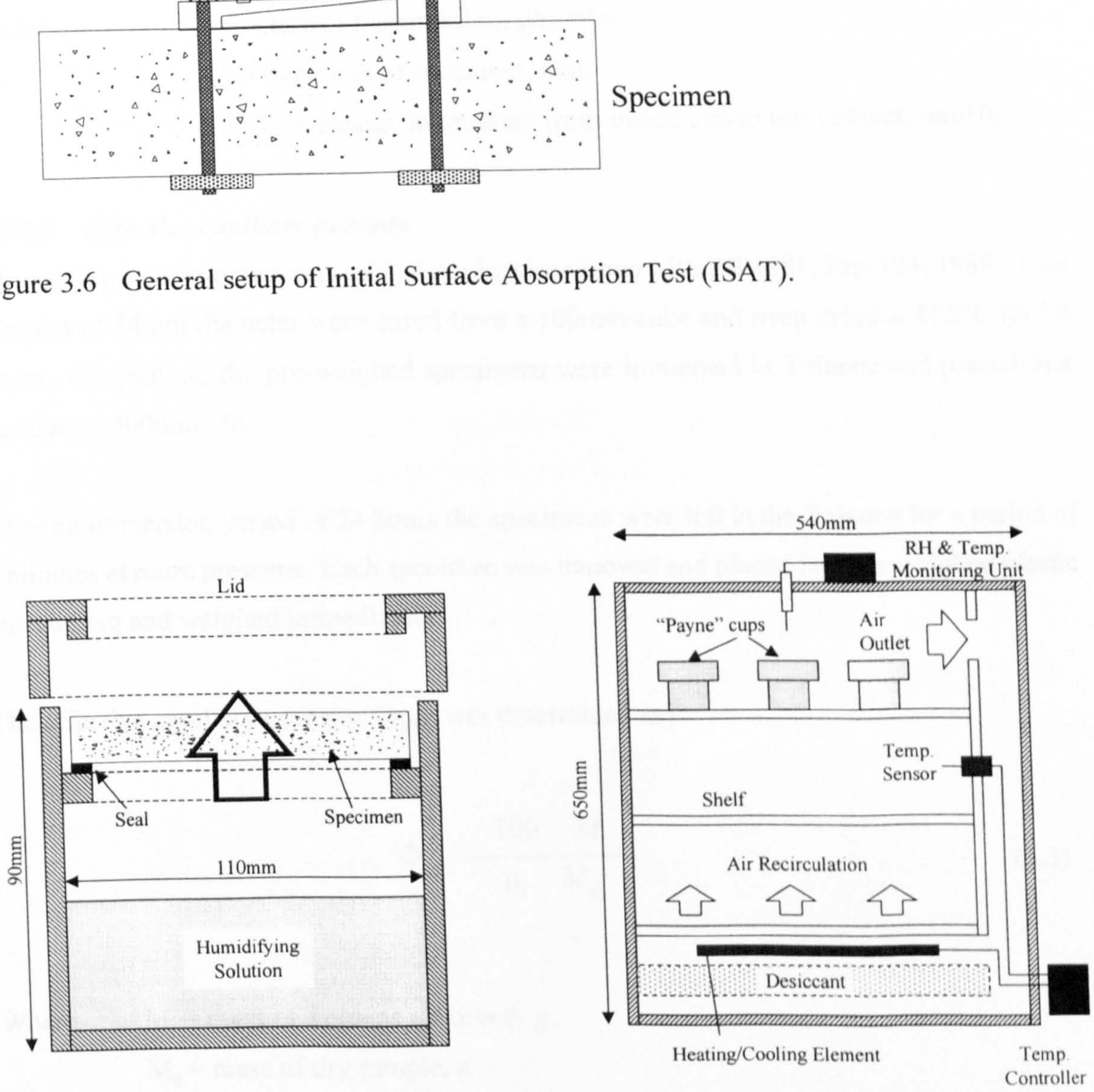


Figure 3.6 General setup of Initial Surface Absorption Test (ISAT).



(a) (b)

Figure 3.7 Apparatus used in Water Vapour Diffusivity Test. (a) "Payne" cup showing specimen and humidifying solution, (b) Temperature and relative humidity controlled test cabinet.

The cups and specimens were weighed to the nearest 0.001g at 24 hour intervals until a steady rate of vapour flow was achieved, ie constant weight change over 3 consecutive 24 hour periods. The coefficient of water vapour permeability (k) is calculated using Darcy's law as proposed by Dhir et al (1989c):

$$k = \frac{Fl}{P_1 - P_2} \qquad (3.2)$$

where: F = rate of transmission, g/mm².s

l = thickness of specimen, mm

P_1-P_2 = change in pressure from inside cup to test cabinet, mmHg

3.6.2.3 Effective capillary porosity

The capillary porosity test was carried out in accordance with BS 1881: Part 124: 1988. Two samples of 54mm diameter were cored from a 100mm cube and oven dried at 105°C for 24 hours. On cooling, the pre-weighed specimens were immersed in Toluene and placed in a vacuum at 500mm Hg.

After an immersion period of 24 hours the specimens were left in the Toluene for a period of 5 minutes at room pressure. Each specimen was removed and placed in a pre-weighed plastic airtight bag and weighed immediately.

The effective capillary porosity (Φ_{eff}) was determined as:

$$\Phi_{eff} = \frac{100 \cdot M_t}{\rho_t \cdot M_d} \qquad (3.3)$$

Where M_t = mass of Toluene absorbed, g

M_d = mass of dry sample, g

ρ_t = relative density of Toluene

The capillary porosity was taken as the equivalent mass of water required to fill the pores and expressed as a percentage of the dried specimen mass to the nearest 0.1%.

3.6.2.4 Intrinsic air permeability

Intrinsic air permeability was determined by a method developed at the University of Dundee (Dhir et al, 1989a). A 54mm diameter core was extracted from a 100mm cube at the appropriate test age. The core was then cut to provide two 50mm long samples which were oven dried to a constant weight at 105°C.

Before positioning the specimens with the as cast face facing the inlet air, a liberal layer of grease was applied to the edges to enhance the sealing, avoiding leakage. The precise length of the specimen was measured on three lengths using calipers. The uniaxial air pressure was applied by means of a compressor up to the maximum inlet pressure of 2.76N/mm^2. The air was filtered of oil and other debris and dried to a relative humidity of approximately 0.1%.

Upon achieving air flow equilibrium through the specimen at the prescribed inlet pressures, the inlet and outlet pressures were recorded. The prescribed inlet pressures used were 30, 50, 70, 90 and 110 psi, applied in an ascending order (0.21N/mm^2 to 0.76N/mm^2 in 0.14N/mm^2 increments). The outlet pressure, measured in cc/min was taken after 5 minutes for each inlet pressure when steady state conditions had been achieved.

The intrinsic air permeability (k) was determined using the following equation:

$$k = \frac{2\mu L P_2 Q}{A(P_1^2 - P_2^2)} \qquad (3.4)$$

where
Q_2 = outlet volume rate of flow (cc/min)
P_1 = inlet pressure (psi)
P_2 = outlet pressure (atmospheric)
A = cross-sectional area of specimen (mm^2)
L = length of specimen (mm)
μ = dynamic viscosity of air

The k value is then corrected for gas slippage by plotting the k obtained from the equation above aginst 1/ P_m where:

$$P_m = \frac{(P_1 + P_2)}{2} \qquad (3.5)$$

and the straight line extrapolated to infinite pressure (ie $1/P_m = 0$). This gave the intrinsic air permeability (k) corrected for gas slippage.

3.6.3 CEN Simulated Natural Carbonation Test

The simulated natural carbonation test method was developed from the draft CEN test method (CEN, 1997). The principal of the test method is that concrete specimens are stored in an atmosphere of CO_2 content of 0.03-0.04% by volume, a temperature of 20°C±2°C and a relative humidity of 65±5%. Three exposure classes have been defined to account for the variations in atmospheric moisture conditions. Details of the original CEN draft and the development of the test method are outlined in Chapter 4. The methodology of the enhanced test is given in Appendix A.

3.6.4 Accelerated Carbonation Test

The accelerated carbonation test was developed previously at the University of Dundee by Dhir et al (1986). The principal of the test is that concrete is exposed to an increased partial pressure of CO_2 in order to accelerate the carbonation process.

The test specimens used were concrete prisms of 510x100x100mm. After 24 hours in the mould and under a tent of hessian, the specimens were conditioned in sealed air tight polythene bags for a further 27 days. On removal from the bags, specimens were air dried for 24 hours at 20°C in the laboratory so that the influence of the moisture content on the carbonation rate was minimised.

Four faces of the specimen were coated with 5mm of paraffin wax to leave two longitudinal faces exposed before transferring to the accelerated carbonation test chamber. The test chamber had a partial pressure of CO_2 of 4% ± 1%, a temperature of 20°C ±2°C and a relative humidity of 55% ± 5%. A schematic of the test chamber is shown in Figure 3.8.

At various test ages, a 50mm thick slice was split from the prism and tested with a phenolphthalein solution in accordance with the RILEM method (RILEM, 1988). The split face was divided into eight sections and the five central points taken as the measurement points. This closely resembled the measurement method as used in the CEN carbonation test and is shown in Figure 3.9. This gave a total of ten carbonation readings for each specimen at each test age.

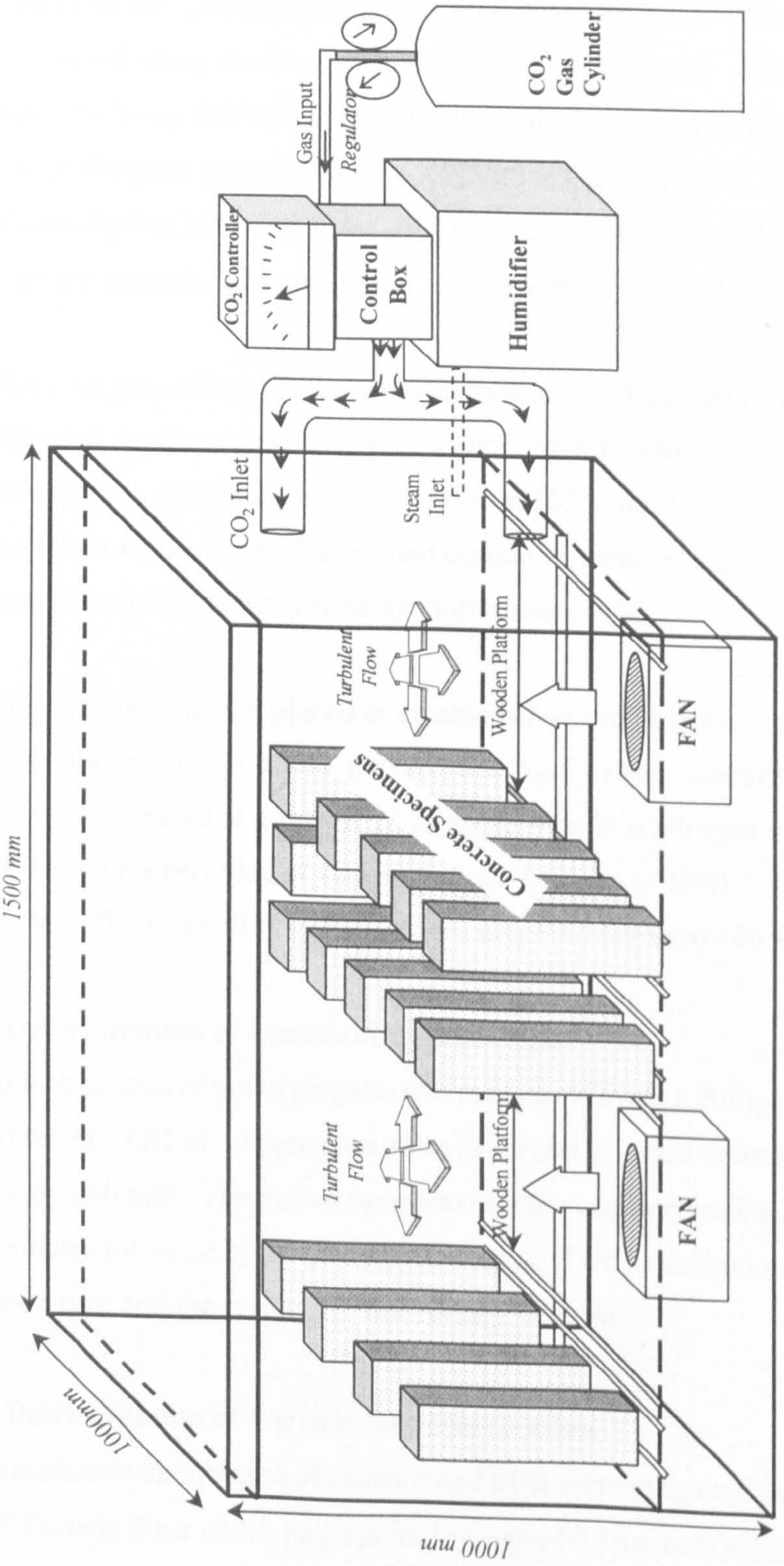


Figure 3.8 Schematic of accelerated carbonation test chamber previously developed at Dundee University (Abbas, 2000).

Between testing the specimen for carbonation and returning it to the accelerated carbonation chamber, the split end was sealed with a layer of paraffin wax to prevent longitudinal carbonation within the specimen.

3.6.5 Thermogravimetric Analysis

Assessment of the calcium hydroxide, $Ca(OH)_2$, of the outer 10mm of the concrete samples was conducted using thermogravimetric (TGA) techniques. This method was adopted in preference to X-ray diffraction (XRD) due to the problems associated with identifying and quantifying the peak produced on the XRD trace (Taylor, 1997). These problems arise since the calcium hydroxide tends to be deposited in a poorly crystalline form when pozzolanic materials are present. The equipment is shown in Figure 3.10.

Samples were ground from the concrete surface using a hand held profile grinder. The samples were taken at depths of 0.5, 1, 2, 4, 6, 8 and 10mm to allow a $Ca(OH)_2$ profile to be drawn. Prior to grinding, specimens were oven dried at 105°C until constant weight was achieved and then cooled in a desiccator. The ground sample was then placed in a planetary ball mill for 20 minutes before being hand ground by mortar and pestle.

A 10 mg sample was then placed in an aluminium crucible and placed within the furnace of the TGA equipment. Alumina powder was used as the standard. The temperature of the furnace was increased at a rate of 20°C per minute in a nitrogen atmosphere and the weight loss of the sample recorded at various temperatures up to 1000°C. The $Ca(OH)_2$ content was measured by the proportion of weight loss recorded between 400°C and 450°C.

3.6.6 Determination of Chemical Composition

The bulk oxide analysis of aggregates was carried out using a Philips PW1410 sequential X-ray Spectrometer (XRFS). Aggregates were dried and crushed before milling for 20 minutes in a planetary ball mill. The milled samples were then compressed in a mould at a load of 5 tons for 2 minutes followed by 10 tons for 4 minutes. Two identical samples were tested for each aggregate type and the results are the average of these.

3.6.7 Determination of Particle Size Distribution

The particle size distribution of cements and filler were measured using a Malvern Mastersizer Type E Particle Sizer which had a particle range of 0.1μm to 600μm, illustrated in Figure 3.11.

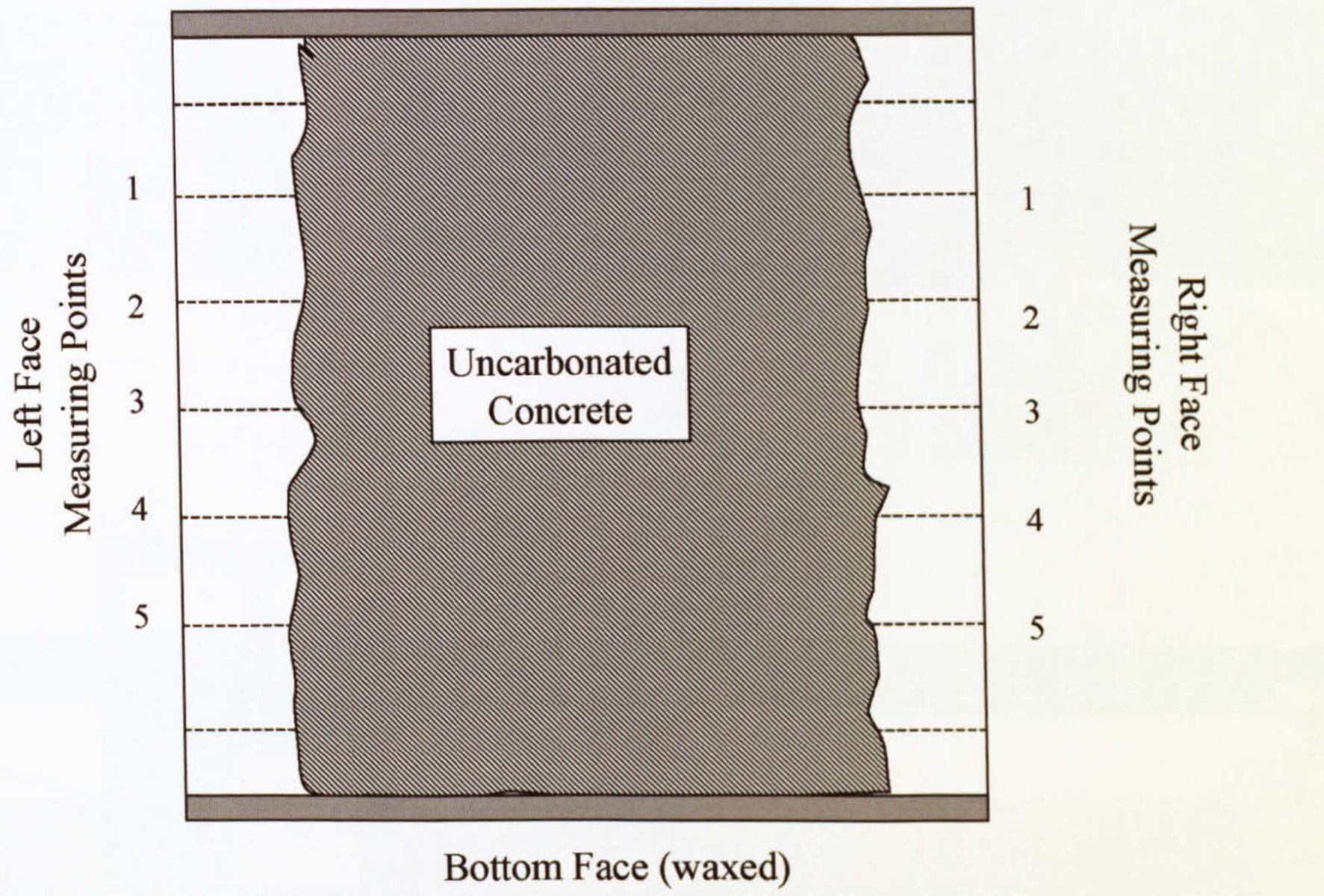


Figure 3.9 Measurement of carbonation depth on split surface of accelerated test specimen.

Figure 3.10 Thermogravimetric Analysis equipment

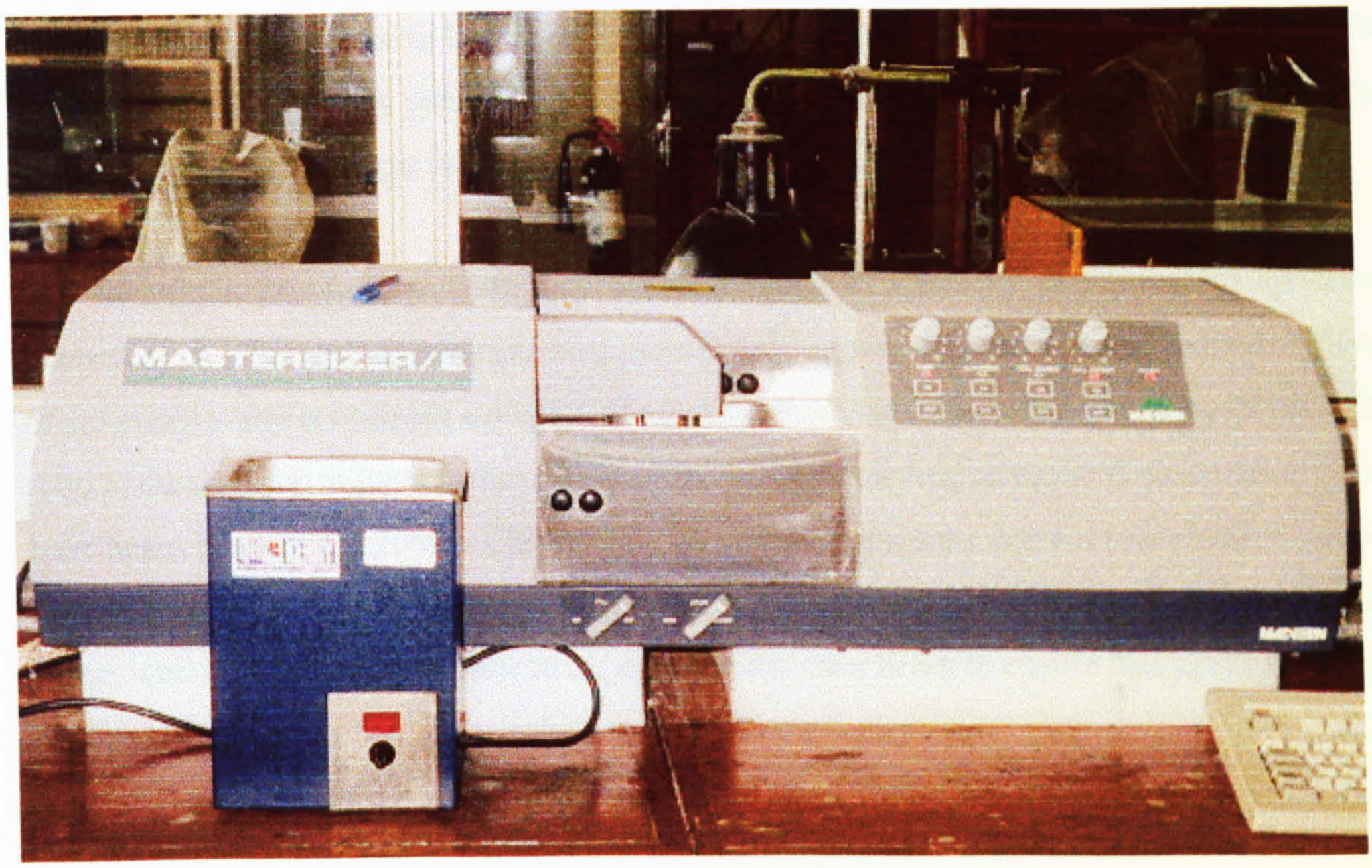


Figure 3.11 Malvern Mastersizer equipment for particle size distribution analysis

The principles of particle size calculation are based on low angle laser scattering. A low power Helium-Neon laser is used to form a collimated and monochromatic beam of light which is the analyser beam. Particles presented to the beam will scatter it and a detector measures the integral scattering of all particles simultaneously.

The technique provides particle size characteristics determined as equivalent spherical diameters. A representative sample of approximately 1g was dispersed in approximately 50ml of deionised water containing a dispersive agent, in this case sodium hexametaphosphate. The ratio of the material to the solution was determined by achieving an optimal obscuration of the laser beam (essentially 20%). The optimal obscuration ensured that a representative sample was obtained and that no interference from scattered light from other particles was occurring. Ultrasound was also applied prior to exposure to the laser beam to ensure disagglomeration of particles.

CHAPTER 4

DEVELOPMENT OF A SIMULATED NATURAL CARBONATION TEST METHOD

4.1 BACKGROUND

Concrete durability has traditionally been specified in terms of bulk engineering properties. Standards for structural concrete stipulated maximum and minimum cement contents, a minimum concrete grade and maximum water/cement ratio. Along with a specification for minimum cover, these limiting engineering properties were deemed sufficient to provide adequate concrete durability and provide a satisfactory service life (Somerville, 1986).

Within the past 10 years, an increasing number of new cement types have become available in Europe. The physical and chemical characteristics of these cements are somewhat varied and hence exhibit different hydration characteristics and hydration products. The long term performance of many of these cements is relatively unknown and specifying limits on bulk engineering properties may not be the most economical proposal.

With the current move towards developing performance related test methods by CEN, a joint Working Group (TC51/WG12) was established to investigate the development of performance tests for the prevention of corrosion of steel reinforcement in concrete. TC51/WG12 decided to concentrate on carbonation induced reinforcement corrosion and the development of a test method to determine the performance of concrete in a carbonating environment. In addition, the task group raised the question of whether it was possible to relate the results obtained under non corrosive conditions to conditions under which normal corrosion would occur.

As a result, a draft method was developed using the RILEM procedure for measuring the depth of carbonation (RILEM, 1988) and was subjected to an inter-laboratory Round-Robin series of tests to measure its repeatability (CEN 1997). The indicated precision from these tests was, however, poor and consequently there was no subsequent agreement to publish the test method as a draft for development (ENV) ahead of a full European Standard (EN). However, it was felt that the draft method did provide a first step towards the development of an agreed standard test procedure and was subsequently published as a CEN Report (CEN 1997).

4.2 REVIEW OF DRAFT CEN TEST METHOD

As the corrosion of reinforcement in concrete is a two-stage process, an initiation period and a propagation period, performance criteria should take into account the duration of both. (Tuutti, 1982). Much of the research on carbonation carried out in the past has focussed on conditions where optimum carbonation occurs and there is no potential for corrosion, ie the propagation period is infinite. These conditions, typically at a temperature of 20°C and a relative humidity (RH) of 65%, are common standard laboratory conditions and are also found in the RILEM recommendation CPC-18 "Measurement of hardened concrete carbonation depth" (RILEM, 1988). The main area of concern with the CEN draft test was the conversion of these results to some performance criteria where corrosion may occur. Specified exposure conditions in standards have changed considerably throughout the years with regard to specifying against durability. The latest developments in BS EN 206-1 have moved towards Exposure Classes for different types of deterioration mechanisms and, in the case of carbonation induced corrosion, varying degrees of moisture availability to the concrete.

Table 4.1 gives the characteristics of the initial draft CEN Test. The basic principle of the test method is that concrete is stored in an environment of 350±50ppm CO_2, 20±2°C and 65±5% RH over a period of at least 1 year. At specific ages, a slice is broken from the test prism and the depth of carbonation measured by spraying phenolphthalein on the exposed surface. These conditions were not ideally suited to the corrosion of steel reinforcement, therefore a second storage condition was introduced. The test specimens were placed under water for a period of 6 hours every 28 days to increase the degree of pore saturation in an attempt to replicate the degree of pore saturation which may be experienced in different local microclimates. This, in turn, would yield different rates of carbonation (BRE 1995, Parrott 1987, Hobbs et al 1998).

The CEN test method adopts the recommendations of RILEM CPC-18 (1988) to measure the depth of carbonation, that is, direct measurement of the neutralised depth of cover using a sprayed solution of phenolphthalein indicator.

4.3 PAN EUROPEAN CEN ROUND-ROBIN TEST PROGRAMME

4.3.1 Background

Seven European laboratories took part in this test programme and three test series were conducted. The analysis carried out by CEN/TC51/WG12/TG5 aimed to determine the feasibility of using the test method and ascertain whether repeatable and reproducible results could be obtained.

Table 4.1 Key requirements of the initial draft CEN test method for determining carbonation (CEN, 1997).

Specimen Size	2 off concrete prisms: 100x100mm and ≥400 mm long.
Initial Curing	24 hours under hessian and impermeable plastic sheeting and 3 days uncovered in the mould.
Storage Conditions	
Class 1:	Temperature: 20±2°C . Relative Humidity: 65 ± 5%. • CO_2 Concentration: 350 ± 50 ppm.
Class 2:	As Class 1 but immerse test prisms in water every 28 days for 6 hours.
Test Ages	28, 91, 182, 273 and 364 days ±2% after commencement of storage.
Method of Measuring Depth of Carbonation	50mm slice broken from prism and phenolphthalein sprayed on freshly broken surface. Measurement made by taking the average of 5 readings made on each face.
Reporting of Depths of Carbonation	Average carbonation depths from the two specimens to be reported for each exposure class.

• Typically measured using a wet and dry bulb whirling hygrometer. A complimentary measuring device is to note the evaporation of water from the surface of a water-filled bowl. A RH of 65±5% should correspond to an evaporation rate of 60±30g/m^2.hr.

4.3.1.1 Test Series 1

Test Series 1 consisted of each laboratory manufacturing two groups of four different types of concrete using local aggregates. The cements were supplied by four of the participating laboratories. The test series was designed to determine the variability associated with the composition of the concrete as a whole and of each single specimen, influence of aggregate type, batching and homogeneity of concrete. This series also gave an indication of the variability linked to the type of mixing, degree of compaction, manufacturing environment and initial curing.

Further details can be found in the CEN Report (CEN, 1997) however the four cement types were as follow:

i) Type CEM I - Portland Cement
ii) Type CEM III-A -Blastfurnace Slag Cement
iii) Type CEM IV - Pozzolanic Cement
iv) Type CEM II-L - Limestone Cement

For each of the cement types, two mixes were cast

a) water/cement ratio = 0.70, cement content = 240kg/m^3
b) water/cement ratio = 0.55, cement content = 305kg/m^3

Compressive strength at 28 days was determined on concrete cubes and carbonation depth on concrete prisms at different ages. Two storage regimes or "Exposure Classes" were tested as detailed in Table 4.1. For the purpose of brevity within the current study, analysis of Exposure Class 1 data only is presented herein.

4.3.1.2 Test Series 2

This test series consisted of a single laboratory manufacturing concrete specimens and distributing two specimens to each laboratory at an age of 14 days. These were stored in Exposure Class 1 only. The concrete mix had a cement content of 330kg/m^3 and a water/cement ratio of 0.50. The cement type was a CEM III/B blast furnace slag. Test Series 2 was designed to obtain the repeatability and reproducibility values which do not take account of the variability associated with the manufacture of the concrete. The results only consider the variability of the carbonation test and the effect of the variation in storage conditions.

4.3.1.3 Test Series 3

Test Series 3 consisted of 1:1 scale photographs of concrete that had been subjected to carbonation and sprayed with phenolphthalein indicator to display the carbonated area. One laboratory performed the test and sent photographs of two different concrete types to the other partners who measured the depth of carbonation on the scale photographs. This test series determined the variability of the method of measuring the depth of carbonation, albeit under different conditions from the real method, ie on photographs, as opposed to on actual test specimens.

4.3.2 Analysis of Pan European Round Robin Data

Table 4.2 shows the variation in storage conditions reported by the participating laboratories. Two of the seven laboratories did not conform to the CEN Test limits in both the CO_2 content and relative humidity. Across the seven laboratories, the coefficient of variation, V, was measured as 33% for CO_2 content and 12% for the RH. This was deemed to be unacceptable by CEN and was assumed to contribute significantly to the variation of the test results.

The Table also shows the relatively large degree of variation in the measured 28 day compressive strength experienced in Test Series 1. In most cases the coefficient of variation across the seven laboratories was greater than 10%. The wide range in compressive strengths was attributed to the fact that in some cases, water/cement ratios were increased slightly in order to achieve the desired workability. The manufacture of nominally similar concrete was also found to vary due to the varying shapes of aggregates produced from different sources. It was also noted that early curing conditions varied form laboratory to laboratory and this was found to have a profound effect on the carbonation resistance of the concrete.

Inevitably, in Test Series 1, variations in 28 day compressive strength led to large variations in carbonation depths, as indicated in Table 4.3. In all cases, at 1 year the coefficient of variation was greater than 15% and in most cases greater than 30%. This was very high as the standard deviation on average was 2.5mm.

In Test Series 2, variability was somewhat less. For all concrete measured in the Test Series, the standard deviation was found to be 1.0mm, a variation of 12%. The variations in this test series were associated with the differences in storage conditions, since manufacture and initial curing were carried out in the same laboratory.

Table 4.2 Summary table of storage conditions and Test Series 1 28 day compressive strength for Round Robin Results (CEN, 1997).

Laboratory	Storage Conditions				Test Series 1 [1] 28 day Compressive Strength, MPa							
					CEM I		CEM II-L		CEM III/A		CEM IV	
	CO_2, ppm	Temp, °C	RH, %	Evap., g/m².hr	0.55	0.70	0.55	0.70	0.55	0.70	0.55	0.70
Austria	600[2]	20	70	14.1[2]	41	26	38	27	50	37	60	43
France	400	22	70	nd*	33	22	31	23	36	28	36	30
Germany	320	20	65	16.5[2]	39	26	37	27	45	33	51	39
Italy	400	20	55[2]	17.6[2]	37	23	37	26	44	29	48	32
Netherlands	200[2]	20	65	19.0[2]	33	21	35	26	43	30	48	34
Sweden	300	20	65	59.5	41	26	36	27	48	33	53	38
United Kingdom	400	20	50[2]	15.3[2]	28	18	28	21	35	32	43	30
Mean	*374*	*20.3*	*63*	*23.7*	*36*	*23*	*35*	*25*	*43*	*32*	*48*	*35*
SD[3]	*124*	*0.7*	*7.5*	*17.6*	*5*	*3*	*3*	*2*	*5*	*3*	*7*	*5*
V %[4]	*33.0*	*3.7*	*12.0*	*74.6*	*13.0*	*12.0*	*10.0*	*9.0*	*12.0*	*9.0*	*15.0*	*13.0*

* nd = no data was given in report

(1) Concrete cast in own laboratory using local aggregates and cements supplied by Swedish, German, French and Italian partners

(2) Note: Does not conform with CEN requirements.

(3) SD = standard deviation

(4) Calculations of coefficient of variations made by author.

Table 4.3 Summary table of 1 year depths of carbonation for Test Series 1, 2 and 3 Round Robin Test (CEN, 1997).

Laboratory	1 year Carbonation Depth (mean of two prisms), mm										
	Test Series 1 [1]								Test Series 2 [2]	Test Series 3 [3]	
	CEM I		CEM II-L		CEM III/A		CEM IV		w/c ≈ 0.50	Photo 1	Photo 2
	0.55	0.70	0.55	0.70	0.55	0.70	0.55	0.70			
Austria	3.0	6.0	7.0	11.0	9.0	13.5	5.5	9.5	7.8	3.3	9.6
France	1.0	3.5	4.0	8.0	5.0	7.0	3.0	6.0	9.0	3.6	9.8
Germany	3.5	5.5	6.5	10.0	11.0	14.0	5.1	8.0	7.8	3.6	10
Italy	5.5	10.0	11.0	14.0	14.5	21.0	7.5	13.5	10.0	3.6	10
Netherlands	2.5	5.0	7.0	9.0	6.5	10.0	5.1	8.0	8.9	3.8	9.8
Sweden	2.5	6.0	6.5	9.5	10.0	13.5	4.0	7.0	8.3	3.9	11
United Kingdom	4.5	9.5	9.5	12.0	14.5	17.5	9.0	14.0	10.5	4.3	9.7
Mean	*3.2*	*6.5*	*7.4*	*10.5*	*10.1*	*13.8*	*5.6*	*9.4*	*8.9*	*3.7*	*10*
SD	*1.4*	*2.2*	*2.1*	*1.9*	*3.4*	*4.2*	*1.9*	*2.9*	*1.0*	*0.3*	*0.4*
V % [4]	*42.3*	*33.9*	*28.5*	*17.8*	*33.5*	*30.8*	*33.7*	*30.8*	*12.0*	*8.5*	*3.5*

[1] Concrete cast in own laboratory using local aggregates and cements supplied by Swedish, German, French and Italian partners

[2] Concrete cast at one laboratory then sent to other laboratories after 14 days (3 days in the mould followed by 11 days in lab. air)

[3] Measurements from 1:1 scale photographs taken of a concrete manufactured and sprayed with phenolphthalein in a single laboratory.

[4] Calculations of coefficient of variations made by author.

The low coefficient of variation in Test Series 3 confirmed the findings of RILEM CPC-18 in that method of measurement of carbonation depth by means of the phenolphthalein solution has a satisfactory repeatability and reproducibility.

An in depth statistical analysis of the Round Robin Test results was carried out by CEN to examine the repeatability and reproducibility of the test method. Further details of this can be found in the CEN Report on the Round Robin Test (CEN, 1997). The conclusions established that in Test Series 1 the repeatability of the test was satisfactory, however the reproducibility was poor and became poorer with increasing depth of carbonation. Normal variations ie random errors, were unavoidable. However a number of factors were identified as being the main driving force behind variability in test results. These were identified as (CEN, 1997):

1. Diversity between concrete compositions - eg w/c ratio, aggregate type.
2. Different methods of concrete production - eg mixer type, mixing procedure.
3. Difference in methods of specimen production - eg degree of compaction.
4. Conditions and length of early curing.

The reproducibility in Test Series 2 was better than in Test Series 1 although it was still unsatisfactory. The factors leading to the variability in Test Series 2 were identified as :

1. Differences in CO_2 content within storage area.
2. Differences in temperature within storage area.
3. Differences in relative humidity within storage area.

The fundamental conclusion from the Round Robin test programme was that the draft CEN Test could be modified somewhat to provide the groundwork for a performance based test for the carbonation resistance of hardened concrete.

4.4 CONFORMANCE OF TEST STORAGE ENVIRONMENT TO CEN LIMITS

Test Series 2 from the Round Robin identified the need to reduce the variability in the environmental storage conditions. In order to improve the reproducibility and repeatability experienced, it was necessary to investigate the variation observed within a typical laboratory environment.

4.4.1 Storage Condition E1: Typical Laboratory Environment

The typical environmental conditions experienced within the laboratory were measured over a period of 1 month. CO_2 was measured by means of a portable CO_2 monitor. Temperature and RH were measured using an electronic hand held monitor with an accuracy of ±0.5°C and ±0.5%. The monitor was calibrated by testing with a whirling hygrometer, and temperature calibrated against a standard laboratory thermometer. The evaporation rate, which also gave an indirect measure of the RH in the laboratory, was measured by weighing the loss of deionised water from a beaker of dimensions 150x100x75mm. The beaker was weighed daily and the evaporation rate expressed in $g/m^2.hr$.

The typical variations within the laboratory environment were large and were attributed to a number of factors. The movement of people within the laboratory contributed to the variations in CO_2, measured at 550 ± 150ppm. Temperature fluctuations, measured as 21 ± 3°C were also attributed to the movement of people within the laboratory combined with the opening and closing of internal and external doors. Large fluctuations in RH were also experienced, being measured as 60 ± 20%. As temperature and RH are interdependent variables, the same factors leading to vicissitudes in temperature contributed to the variations in RH. The evaporation rate within the laboratory environment fluctuated greatly, measured as 85 ± 35$g/m^2.hr$. The normal laboratory environment was therefore deemed unsuitable for use as a storage area for the CEN Test and work was discontinued.

4.4.2 Storage Condition E2: Controlled Climate Room - Temperature and RH

A proprietary storage room situated within the laboratory with active control over temperature and relative humidity was tested for variations in environmental storage conditions. The room, with internal dimensions 2100 x 1900 x 2400mm was filled with dummy concrete specimens to replicate the presence of carbonating concrete specimens within the storage area. This was necessary as the presence of a large surface area of concrete would significantly affect the CO_2 and RH of the storage environment.

The number of specimens present in the room was such that:

- Room volume/concrete specimen volume = 3.7
- Total exposed concrete surface area in room= 125m^2

The room was fully sealed and CO_2, temperature and RH were measured over the period of 1month as in storage condition E1. Figure 4.1 illustrates the variations in CO_2, temperature and RH over the test period. Although it was possible to maintain the required temperature and RH levels as set by CEN, the CO_2 content rapidly depleted. Within approximately 7 days, the CO_2 had reduced from 420ppm to 255ppm. This was mainly attributed to the fact that the large exposed surface area of concrete was consuming the CO_2 which was then reacting with the pore fluids and to a lesser extent the hydration products. No air from the laboratory was allowed to enter the storage room to replenish the CO_2 content.

4.4.3 Storage Condition E2a: Controlled Climate Room - Door Ajar

The conditions in Storage Condition E2a were similar to E2 however the door ($2m^2$) was wedged ajar to a width of approximately 100mm. This was considered a sufficient width to allow replenishment of CO_2 within the storage room and no attempt was made to force an exchange of air between the interior of the storage room and the laboratory.

Figure 4.1 shows that all environmental factors were, at some stage, outwith the limits specified by CEN. Allowing air from the laboratory to exchange with air in the storage room led to rise in overall mean temperature and CO_2 content and a reduction in RH. The evaporation rate was 80 ± 30 g/m^2.hr indicating that with the door wedged ajar, the laboratory air had almost fully replaced the air within the storage room. The temperature and RH conditions were similar to those experience in storage condition E1.

4.4.4 Storage Condition E2b:Controlled Climate Room - Door Open/Closed 48 hr Cycle

Storage environment E2b involved the door being left fully open continually for 24 hours in every 48 hours. Figure 4.1 shows the fluctuations in temperature, relative humidity and CO_2 concentration. Although the mean CO_2 concentration was within the CEN limits, the overall CO_2 still varied outwith those tolerances. Temperature and relative humidity were closer to the limits as stated by CEN although they still did not fully conform.

From the above experimental programme it was clear that active control was required over CO_2 concentration, temperature and relative humidity in order that the environmental storage conditions conformed to those limits stated in the draft CEN Test method.

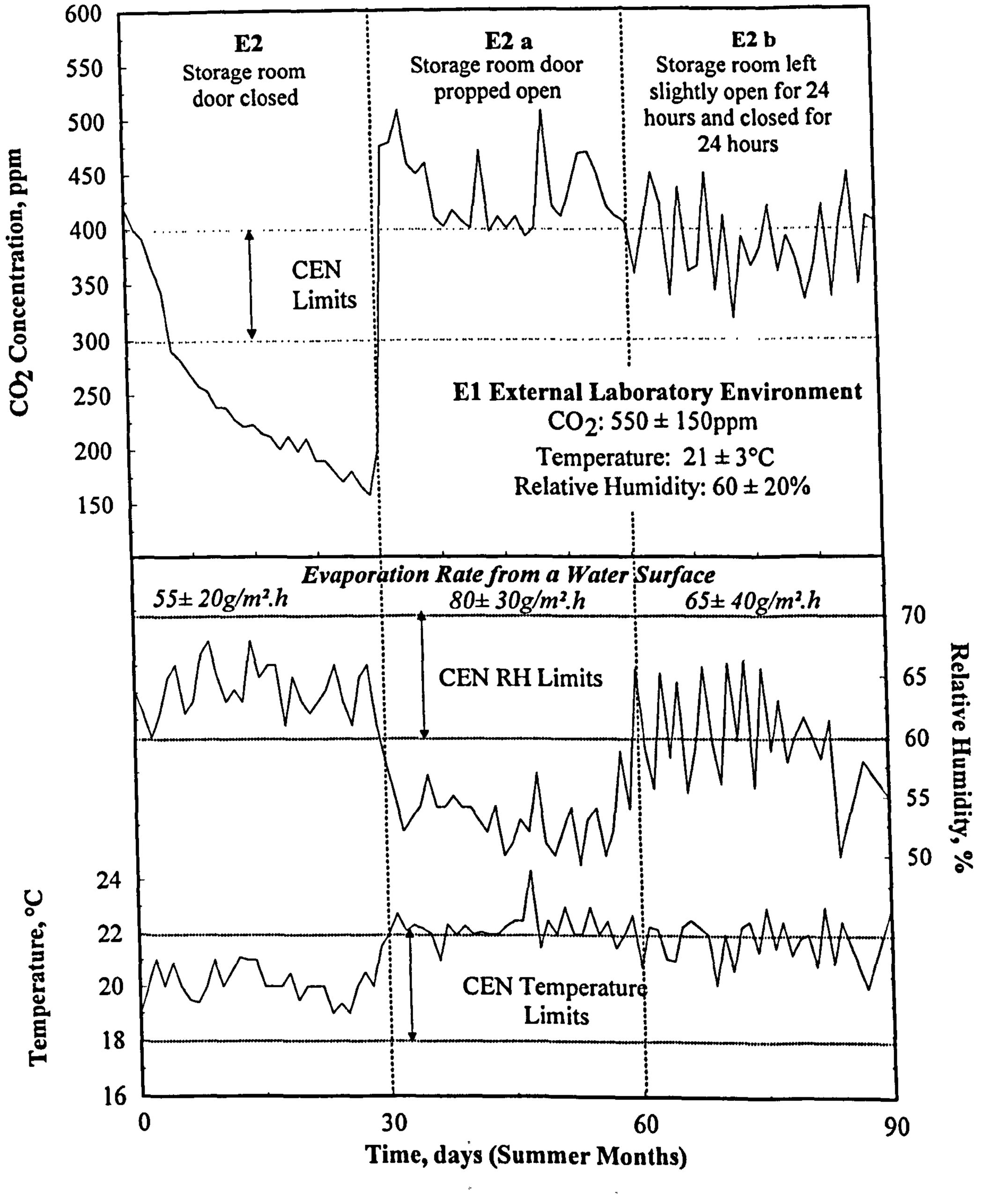


Figure 4.1 Fluctuations of environmental parameters in storage environment E1, E2, E2a and E2b.

4.5 DEVELOPMENT OF ENVIRONMENTAL CONTROL SYSTEM

In order to aid the development of the test method, a number of systems were considered. However, many of the proprietary systems were found to be prohibitively expensive and an in-house system was developed, the primary aims of which were:

- Simplicity of construction.
- Ease of retro-fitting to existing climate rooms.
- Cost effectiveness for use in both academic and industrial sectors.

Figure 4.2 is a schematic diagram of the environmental storage control system developed and retro-fitted to the existing climate controlled storage room. An indicative components list based on 2000 costs (excluding VAT) is given in Table 4.2.

The system consisted of a CO_2 monitor/ controller unit which was a proprietary system based on a non-dispersive infra-red detector and monitor capable of analysing gaseous CO_2 from 0-2000 ppm to an accuracy of ± 5% by volume of full scale deflection, which in this case is 400ppm ± 20ppm. This unit had a built-in air pump which sampled the storage room atmosphere at 1 litre/minute, and an inbuilt recorder port which provided a signal of 0-100 mV DC across full scale deflection. This was used to drive the CO_2 injection unit via DC relays to 2 control valves connected to the bottled CO_2 source. This also allowed visual and sound alarms to be controlled which directly indicated an empty CO_2 bottle. The CO_2 injection unit used signals and a series of relays which operated flow valves allowing a controlled release of CO_2 into the storage room.

The basic electronic operation of the system was designed as follows:

i) The storage room air is constantly monitored by the CO_2 monitor. Air is constantly sampled from the room and tested for CO_2 concentration.

ii) CO_2 concentration is converted from ppm to an equivalent mV with the CEN limits of 300ppm and 400 ppm being set at 20mV and 30mV respectively.

iii) The relay controller receives a mV signal from the CO_2 monitor. If the voltage reading is between 20mV and 30mV, control valve 1 is closed and no CO_2 gas flows into the storage room (NB Control valve 2 is set at open).

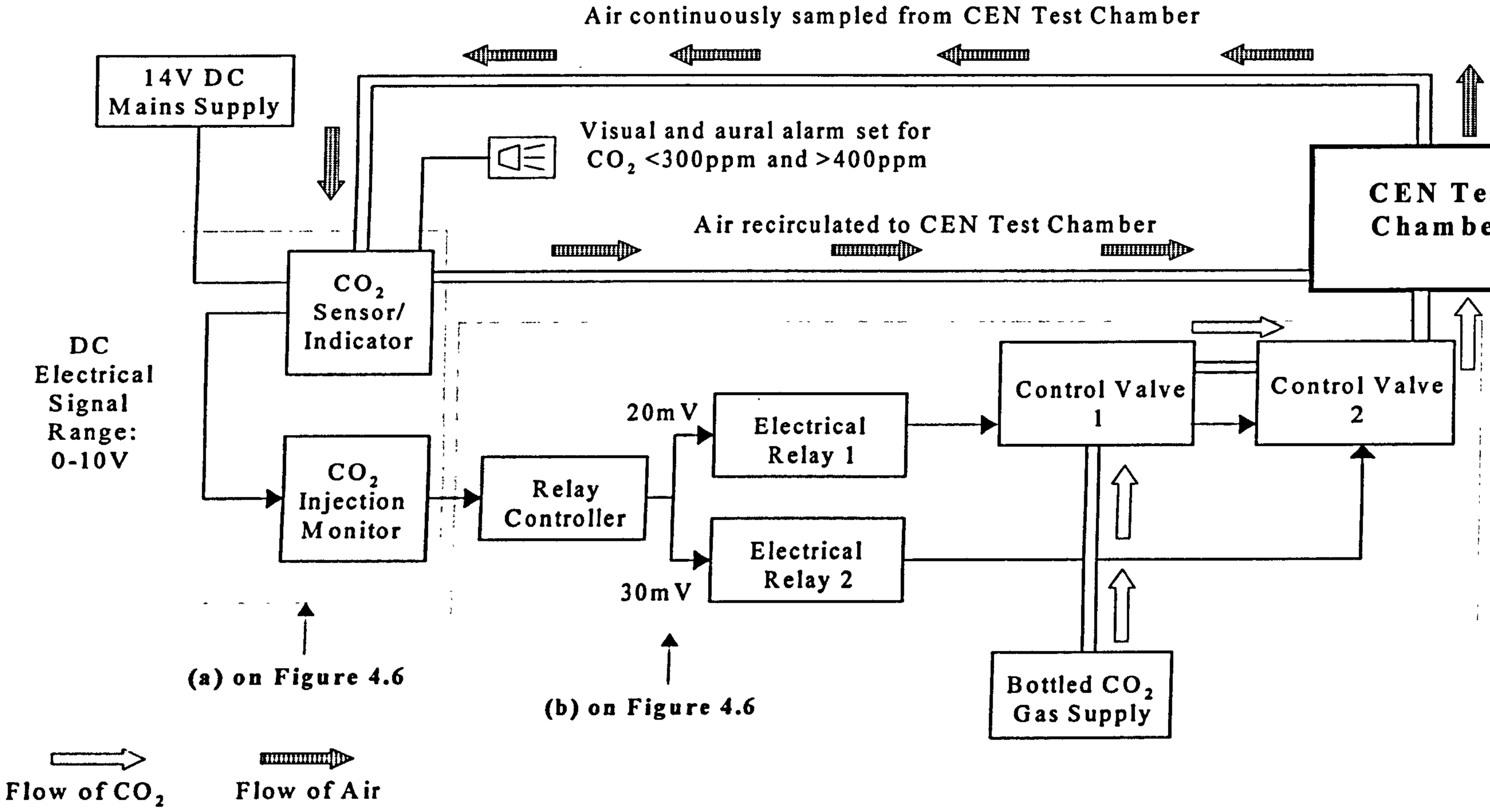


Figure 4.2 Schematic diagram of retro-fitted CO_2 monitor/controller and injection system.

Table 4.4 Component costs of Dundee CO_2 control system.

Component	Cost[1], £
CO_2 Gas	
Operational Liquid CO_2 gas[2]	35
Calibration Gas	55
CO_2 Monitoring	
Proprietary Monitor/controller unit	1750
Electrical Relay Switches , Warning lights etc.	650
Miscellaneous Costs	
Wiring etc.	400
Re-circulation Fans	60
Total Cost[3]	**2950**

(1) 2000 prices excluding local purchase tax (VAT).

(2) 25 kg standard grade. Note: gas bottle rented at £24/month.

(3) This does not include labour costs.

iv) If the voltage falls to 20mV or below, relay 1 opens control valve 1 and CO_2 gas is injected into the storage room until the voltage is between 20mV and 30mV. The proportional valve system is set at 25.5mV such that injection of CO_2 gas will cease when the monitor reads this value.

v) If the voltage rises to 30mV or above, relay 2 closes control valve 2 to prevent further CO_2 gas injection and activates the alarm.

Prior to operation, the system was calibrated using a certified test gas traceable to national standards. For operational purposes standard grade carbon dioxide was supplied from a 25kg bottle which was subsequently found to last approximately 6 months. The concrete test samples were stored on open mesh steel shelving to permit contact with the environment on all sides. This also allowed for the simple removal and replacement of specimens for testing and cyclic wetting and drying in Class 2 and Class 3 exposure.

There was some concern that air would stagnate around the test specimens and result in locally depressed partial pressures of CO_2. Oscillating fans of 27 cm diameter (23 cm blades rotating at 200 rpm) were installed at four points of the room to create a turbulent air flow in the room which was tested using a pigmented indicating air flow powder.

Figure 4.3 shows the interior of the CEN carbonation test chamber. The concrete specimens are placed horizontally on expanded metal shelving to allow the air to circulate freely and for all sides of the specimen to come into contact with CO_2. The Figure also shows the relative humidity being verified using the hand held hygro-thermometer.

The portable CO_2 monitor used to verify the readings taken by the installed CO_2 monitor controller system is shown in Figure 4.4. In the background, the humidifying/dehumidifying apparatus within the CEN Test room is shown. The equipment constantly monitors the RH within the room and this is displayed on the exterior of the room along with the temperature, Figure 4.5.

The CO_2 monitor/controller retro-fitted to the CEN test room is shown in Figure 4.6. The equipment on the left is the proprietary CO_2 monitor system which constantly samples the air in the CEN Test room. The equipment on the right is the in-house system developed to inject the CO_2 into the room, should it be required.

Figure 4.3 Interior of CEN Test chamber showing specimens stacked on mesh shelving. Relative humidity is being verified by means of a hand held hygrothermometer.

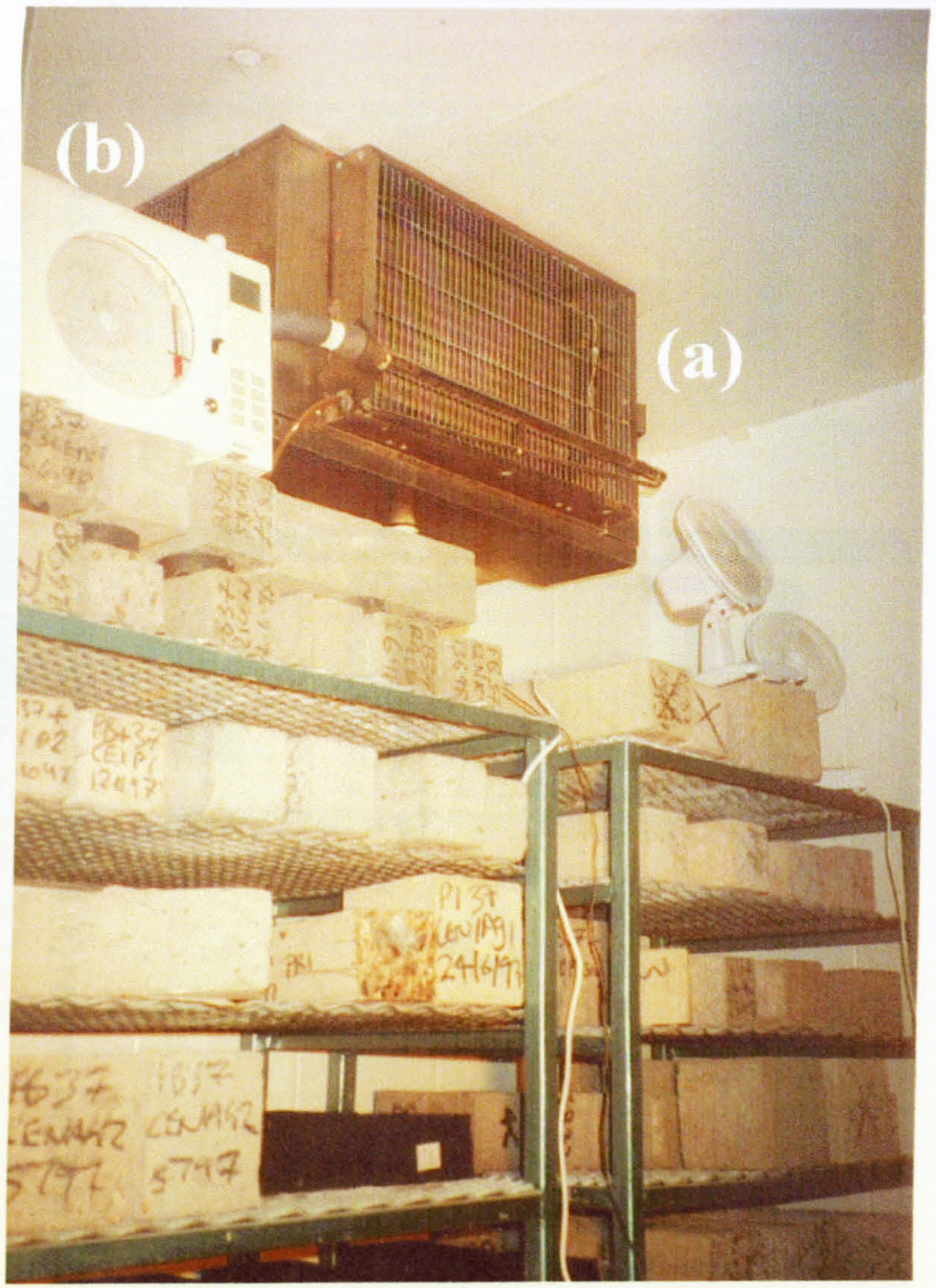


Figure 4.4 Interior of CEN Test chamber showing (a) humidifying/dehumidifying apparatus. CO_2 content is being verified by means of a portable CO_2 monitor (b).

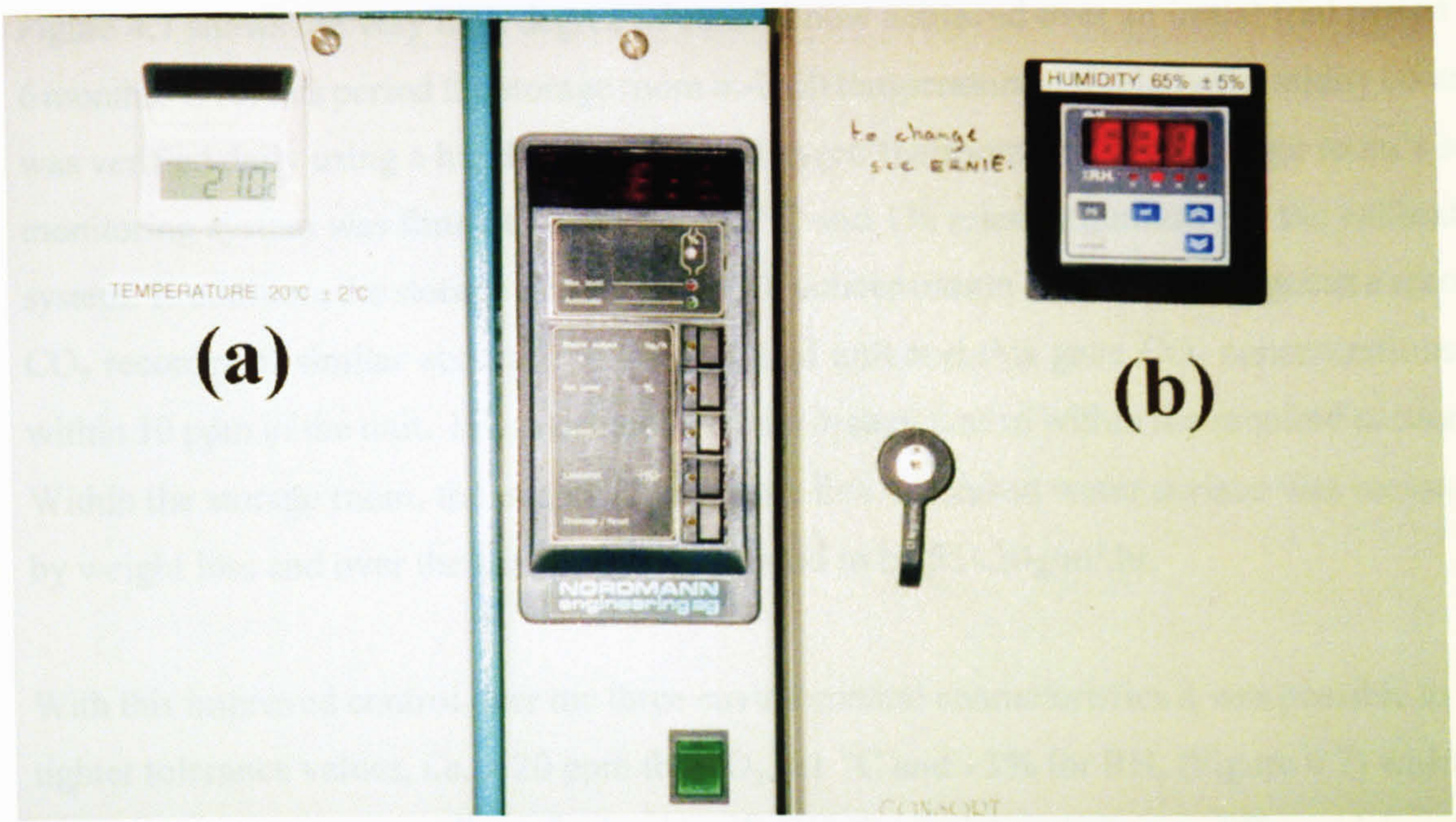


Figure 4.5 Constant monitoring of (a) temperature and (b) relative humidity is possible with external environmental displays.

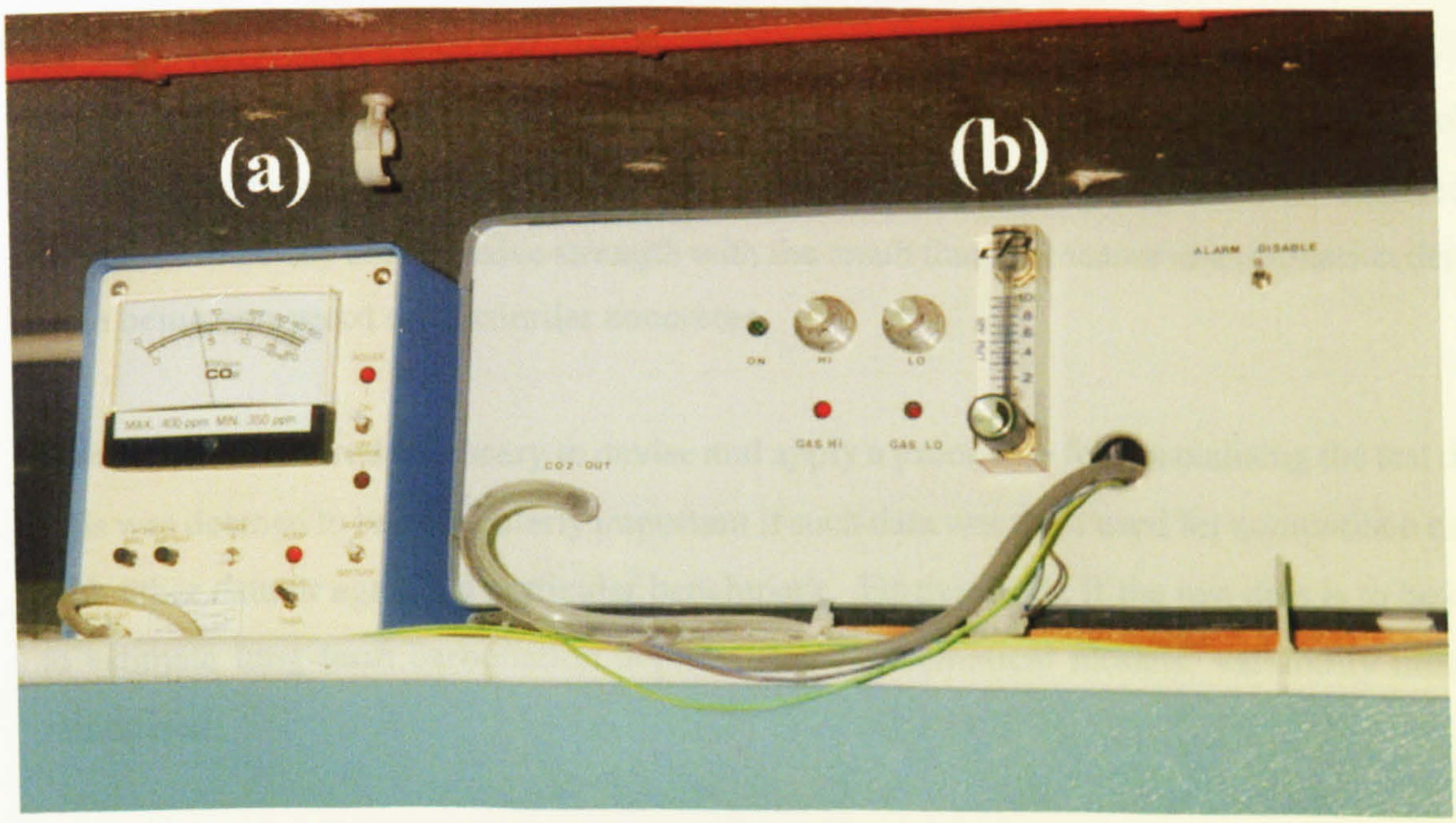


Figure 4.6 Retro fitted CO_2 monitor/controller system. (a) Proprietary CO_2 monitoring system, (b) CO_2 injection system control box and audiovisual alarm.

Figure 4.7 shows the very high degree of control now achieved over an initial trial period of 6 months. Over this period the storage room in-built temperature and relative humidity control was verified daily using a hand held calibrated hygro-thermometer. The storage room's self monitoring system was found to be within 0.5°C and 1% relative humidity of the calibrated system. In addition, the storage atmospheric CO_2 concentration was validated against a second CO_2 recorder of similar accuracy to the installed unit and this gave CO_2 concentrations to within 10 ppm of the unit. It was deemed that the system was to within the required accuracy. Within the storage room, the evaporation from a free deionised water surface was measured by weight loss and over the trial period was found to be 55±20g/m².hr.

With this improved control over the three environmental characteristics it was possible to use tighter tolerance values, i.e. ± 20 ppm for CO_2, ±1 °C and ±3% for RH, (Figure 4.7) which in the longer term, may contribute further in reducing the variation between different laboratory storage conditions. No testing was carried out to determine if these tighter environmental tolerances promoted increased test precision, however this may provide scope for further research.

4.6 NORMALISATION OF CARBONATION DEPTH

The main obstacle leading to the high reproducibility within Test Series 1 of the Round Robin was the fact that different laboratories were manufacturing their own specimens. This led to variations in 28 day compressive strength with the result that the measured carbonation depths were being compared on dissimilar concretes.

It was thus considered necessary to devise and apply a procedure for normalising the test data. This was deemed to be particularly important if such data was to be used for comparison either with other data or against a particular benchmark. Furthermore, if the test data is to be used to estimate long term carbonation depths using mathematical models, variability must be minimised.

The normalisation procedure developed used the following mixes:

i) A *primary mix* was designed to achieve the required concrete grade at 28 days.

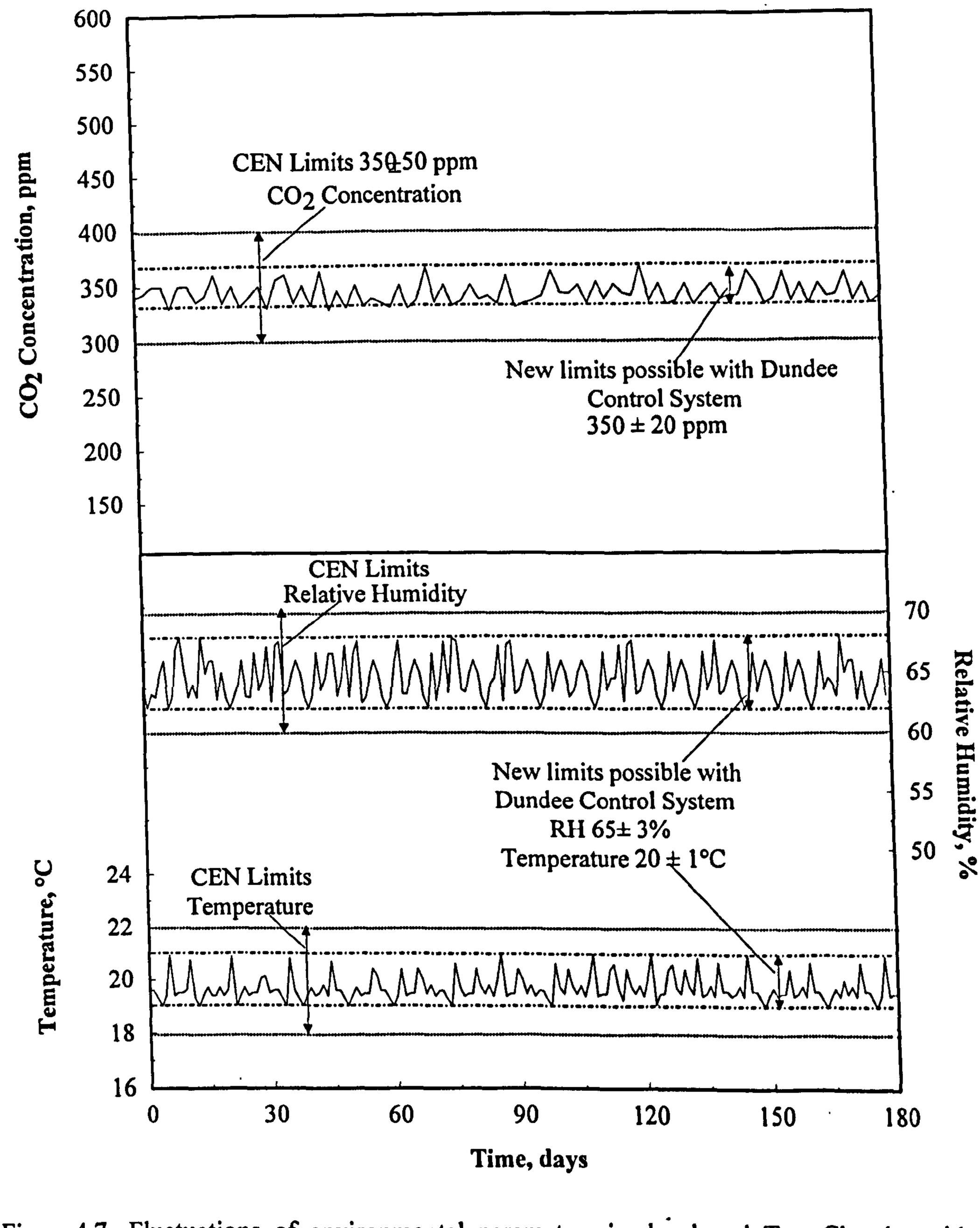


Figure 4.7 Fluctuations of environmental parameters in developed Test Chamber with Dundee environmental control system.

ii) Two *secondary mixes* were also produced with ± 8% by mass of the total cement content of the primary mix. This value was arbitrarily chosen but corresponded to ± 25kg/m³ for this testing programme where a 37 N/mm² PC/30% PFA mix was used. The secondary mixes had the same free water content as the primary mix and were volumetrically adjusted by altering the fine aggregate content.

The test data were then normalised using a two stage procedure to give the exact mix constituent proportions and thereby allow the exact carbonation depth to be determined. The procedure is described below by way of an example, using a 37 N/mm² PC/PFA 30% mix.

Given that many different combination of cement types (having different rates of reaction and hydration and therefore rates of strength development) can be compared using the developed test, it was decided to adopt a single criterion to determine the period of sealed cured storage prior to transfer to the Dundee storage room (Jones et al, 2000). The criterion adopted was that specimens would be seal cured until $0.5f_{cm,28}$ before transference to the test chamber. Given the different hydration rates of the numerous cements on offer, this meant specimens were being subjected to carbonation at a similar grade rather than a similar age.

4.6.1 Normalisation Procedure

4.6.1.1 Stage 1: Determination of normalised mix constituent proportions

In Stage 1 of the procedure, the standard 28 day cube strength is plotted against the cement content as shown in Figure 4.8a. This allows the exact cement content required to achieve a standard 28 day cube strength of 37 N/mm² mix to be determined. In this case this was found to be 374 kg/m³, in comparison to 370 kg/m³ originally batched for the primary mix. Although rounding this figure to 375 kg/m³ for the normalised mix is reasonably similar to the originally batched cement content, it is quite possible, under normal laboratory conditions, to experience a variability in batch measurements or compressive strength in the region of ±8%.

This leads to a possible variation in cement content of 355 to 385 kg/m³. This will have a significant effect on the depth of carbonation, not only at 1 or 2 years but also when predicting longer term carbonation performance.

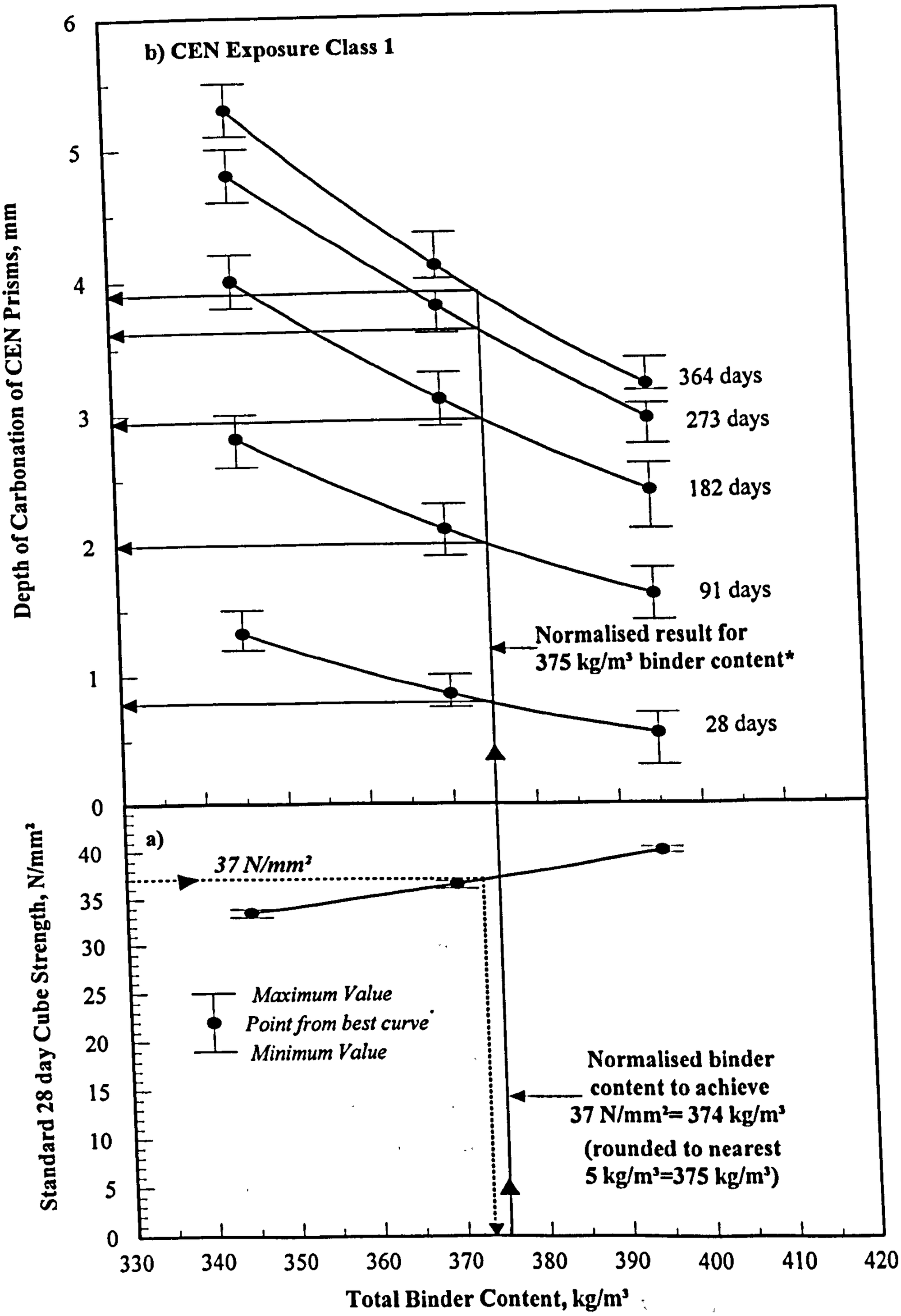


Figure 4.8 Second stage in the normalisation procedure. a) shows determination of exact cement content to achieve a standard compressive strength of 37N/mm² at 28 days.
b) determination of normalised carbonation depths.
(Note: values are rounded to 0.5mm)*

4.6.1.2 Stage 2: Determination of Normalised Carbonation Depth

Having established the normalised mix proportions, it is possible to determine the normalised carbonation depth at any particular test age. The depth of carbonation at the defined incremental storage period is plotted against the total cement content, Figure 4.8b.

The depth of carbonation is determined from the normalised cement content, 375 kg/m³, and subsequently rounded to the nearest 0.5mm. It should be noted that the error bars shown in Figure 4.8b represent maxima and minima of 40 measurements of carbonation depths ie 20 measurements on each test specimen, based on the phenolphthalein test.

Again assuming typical laboratory variability giving rise to 28 day standard strength from 35 to 39 N/mm², it is possible to estimate the likely variation in 1 year CEN carbonation depths. In this case it is estimated that this will result in a potential carbonation depth varying from 3.5 to 4.5 mm which will have implications for prediction of longer term carbonation.

4.7 ADDITIONAL MODIFICATIONS TO TEST METHOD

In addition, the draft CEN test recommended avoiding the use of stripping agents that could subsequently adhere to the concrete after demoulding and potentially impede carbonation. However, it was found after a series of initial tests that without the use of a mould release agent, the test specimens were damaged after demoulding and also had a significant number of blow holes. Both dry silicon and a water-based oil release agent were tested and it was found that the latter produced the minimum build up on the test specimen, particularly as it was possible to wipe the concrete surfaces with an absorbent cloth.

Prior to commencing the study, a further Exposure Class was introduced with an increased wetting/drying frequency. Exposure Class 3 was similar to that of Class 2 however the specimens were stored underwater for 6 hours every 7 days. The purpose was to determine whether the 3 Exposure Classes could be linked to that of the 3 Exposure Conditions in BS EN206-1, namely, Indoors, Outdoor Sheltered and Outdoor Unsheltered.

4.8 REPEATABILITY OF THE DEVELOPED CARBONATION TEST METHOD

A limited series of tests were carried out to assess the effect of proposed modifications to the test. A series of 10 repeated mixes giving 2 sets of test samples were produced, one group of which was subjected to the current draft CEN method testing and the second to the proposed

method of testing, with both series of test samples stored in the Dundee storage room to CEN Class 1 exposure conditions. In addition, for comparative purposes, two further subsets of test samples were stored for 20 weeks in an accelerated carbonation chamber with an atmospheric environment of 4000 ± 500 CO_2 ppm, 50 ±5 % RH and 20 ±2°C. Full details are given by Dhir et al (1985). Table 4.5 compares the results obtained.

Considering the simulated natural results first, it is interesting to note that the mean carbonation levels were exactly the same in both cases. However, the standard deviation and coefficient of variation were around five times lower with the modified test method. Although in this particular case using the t-test to compare these results suggests that the differences were insignificant at a 95% confidence level. However, this may only have been due to the fact that the t-test mainly involves a comparison between the mean values which in this case were exactly the same. Thus, the Chi-squared test was additionally applied to the results.

Using this test and again applying a 95 % confidence level, the Chi-squared test was calculated to be 2.73 (Kennedy and Neville 1976). This suggested that there was a significant difference in the range of individual test results and that the repeatability of the results is significantly improved when the Dundee test procedure was adopted. The only real variation in the new modified test method results was due to the fact that the depths of carbonation were rounded to the nearest 0.5mm.

Since carbonation depths are small after 1 year CEN storage, it was inevitable that any variations could be somewhat masked. The accelerated test results are perhaps a more realistic test for the effects of the normalisation procedure. This is borne out by the results of Table 4.5 and it was found that the t and Chi squared test both suggested significant differences at the 95 % confidence levels.

4.9 SUMMARY

From the study of the current method for the measurement of carbonation depth in hardened concrete it was concluded that two modifications to the test were required in order to reduce the overall variability experienced in the pan European Round Robin test. It was found that it was difficult in typical concrete laboratories to conform concurrently with the storage environment requirements for temperature, relative humidity and CO_2 concentration.

Table 4.5 Repeatability of a 37N/mm^2 PC/PFA 30% mix with one operator in CEN and accelerated carbonation exposures with and without the normalisation procedure.

MIX	Carbonation Depth, mm			
	Without Normalisation		With Normalisation	
	CEN* 364 days	20 weeks[1] Accelerated	CEN* 364 days	20 weeks[1] Accelerated
1	5.5	14.5	4.0	13.0
2	3.0	16.0	3.5	13.5
3	5.0	17.5	4.0	15.0
4	3.0	17.0	3.5	15.0
5	6.0	17.5	4.0	14.0
6	3.0	18.0	3.5	15.5
7	5.5	16.0	4.0	13.5
8	3.0	13.5	4.0	14.0
9	3.0	15.0	4.0	15.5
10	5.0	17.0	4.0	13.5
Maximum, mm	6.0	18.0	4.0	15.5
Minimum, mm	3.0	13.5	3.5	13.0
Mean, mm	4.0	16.0	4.0	14.5
SD, mm	1.3	1.5	0.2	0.9
V, %	31	9	6	6.5
t-test CEN	Insignificant Difference at 95% level			
Accelerated	Significant Difference at 95% level			
Chi-squared Test	7.60[2]	4.86[3]	2.56[2]	0.59[3]

*Including additional Dundee control on storage conditions

[1] 4000 ±500 ppm CO_2, 50 ± 5%RH, 20 ± 2°C

At a 95% confidence level the Chi-squared limit is 2.73[2] for CEN results and 3.94[3] for the Accelerated results (Kennedy and Neville 1976).

This was confirmed in an analysis of the results of a pan European Round Robin test programme in which it was found that only one laboratory had full conformity with the CEN test requirements. The reported statistical variance was significant, leading to variations in Test Series 2 of the Round Robin.

Compliance with the CEN storage requirements could only be achieved by a fully air conditioned sealed room. However, it was necessary to provide actively controlled CO_2 injection in order to maintain the required CO_2 concentration in the room. Significant depletion of atmospheric CO_2 was noted within about 5 days if this was not replenished. As a result, a low cost CO_2 monitor/controller system was designed for retro fitting to suitable storage rooms found in most well equipped laboratories. Using this system it was found that tighter tolerances for storage environment were possible.

A normalisation procedure for the determination of carbonation depth was developed to reduce the variability experienced in Test Series 1 of the Round Robin. Firstly a primary mix and two secondary mixes were used, the latter of which had an alteration to the cement content of ±8% by mass. By plotting 28 day strength against cement content, the normalised cement content required to produce the test concrete with the desired standard cube strength can be determined. Using this value and by plotting cement content against depth of carbonation, the normalised depth of carbonation can be determined at any particular test age. A limited series of repeatability tests were carried out comparing the effect of this two stage normalisation process and it was found that the coefficient of variation was reduced by approximately fivefold. A Chi-squared test also showed that there was an insignificant difference between the depths of carbonation between the repeated mixes.

The fully modified test method is given in Appendix A with modifications to the test method recommended by this study shown in red text.

CHAPTER 5

EFFECT OF CEMENT TYPE ON CARBONATION RESISTANCE

5.1 INTRODUCTION

The harmonisation of concrete standards throughout Europe is reaching a crucial period. The European Standard for cement, BS EN 197-1 allows a number of unfamiliar cement types to be used in structural concrete and, with the development of the European standard for concrete specification, BS EN 206-1, the need to obtain information on the long term durability of these cement types is paramount to the development of performance based design specifications.

The second phase of the current study aimed to appraise the carbonation resistance of selected CEM II concretes containing cements which UK Engineers are currently unfamiliar with. Having identified improvements to the CEN test for carbonation, a number of cement types were studied including PC/PFA, PC/metakaolin (MK) and PC/condensed silica fume (CSF). Full details of the materials and mix proportions are given in Chapter 3.

The concrete permeation characteristics were determined using the initial surface absorption test (ISAT), water vapour diffusivity (WVD), intrinsic air permeability, and capillary porosity tests to observe the effects of the cement type on permeation and subsequent effects on carbonation resistance. The relative performance of the cement types in the three CEN Exposure Classes was also examined to observe the effect of cyclic wetting and drying on carbonation resistance. An accelerated carbonation testing programme was carried out in parallel with the CEN test and the sensitivity of carbonation resistance to changes in mix proportions examined.

5.2 DETERMINATION OF NORMALISED MIX PROPORTIONS FOR 37N/mm²

5.2.1 Normalisation Procedure

The current study had identified that the initial work carried out by CEN (CEN, 1997) using the CEN test for carbonation required a normalisation procedure to improve the overall repeatability of the test method and allow an exact comparison with long term data, or an identified benchmark to be made when testing concrete. Full details of the procedure are given in Chapter 4. Determination of the normalised mix proportions are illustrated here by means

of example, in this case for the PC/PFA30% Reference Mix. The compressive strength development data for all primary and secondary mixes cast is given in Appendix B. Figure 5.1 shows the variability in the standard cured compressive strength development of the primary mixes cast for the cement types to be tested. At 28 days, the range in compressive strength is 35-40N/mm^2, which has the potential to lead to large variations in the carbonation performance of concrete (Hobbs et al, 1998). A comparison of the compressive strength of the primary and secondary mixes for the PC/PFA30% Reference Mix at each test age is given in Figure 5.2 which illustrates that even slight variations in the mix proportions, in this case ±25kg/m^3 cement content, can give rise to notable variability in compressive strength at 28 days.

Table 5.1 gives the mean compressive strength development data for the primary and secondary mixes cast to determine the normalised mix proportions for the PC/PFA 30% Reference Mix. A comparison of the 2/28 day ratio, a factor in BS EN 206-1 which determines the rate of strength development, and, indirectly, the recommended curing period, demonstrates that all mixes would be classified as having a medium strength development. Figure 5.2 and Table 5.1 show that the primary mix, which was intended to give 28 day standard compressive strength of 37N/mm^2, only achieved a strength of 36.5N/mm^{2}in practice. To achieve the required 28 day compressive strength, a cement content of 375kg/m^3 was required. Therefore the original mix proportions for the primary mix were adjusted, Table 5.1. The increase in cement content was accounted for by volumetrically adjusting the fine aggregate content of the mix.

In order to verify that the compressive strength results of the normalised mix proportions were correct, the normalised mixes proportions were cast and tested for compressive strength. Table 5.2 shows that there is little difference in the mean compressive strength obtained from the actual compressive strength results and normalised compressive strength results for PC/PFA 30%. The differences found in the remaining mixes within Test Series 1were also found to be negligible.

5.2.2 Test Series 1 - Normalised Mix Proportions

The normalised mix proportions for Test Series 1 are given in Table 5.3. In all cases the mixes required a slight adjustment to the cement content to achieve the required 28 day compressive strength of 37N/mm^2. As expected, the PC/PFA 30% Reference Mix required the highest cement content in order to offset the higher replacement level of PC and the fact that the pozzolanic reaction associated with PFA is greater after 28 days (Jones and Troy, 1992).

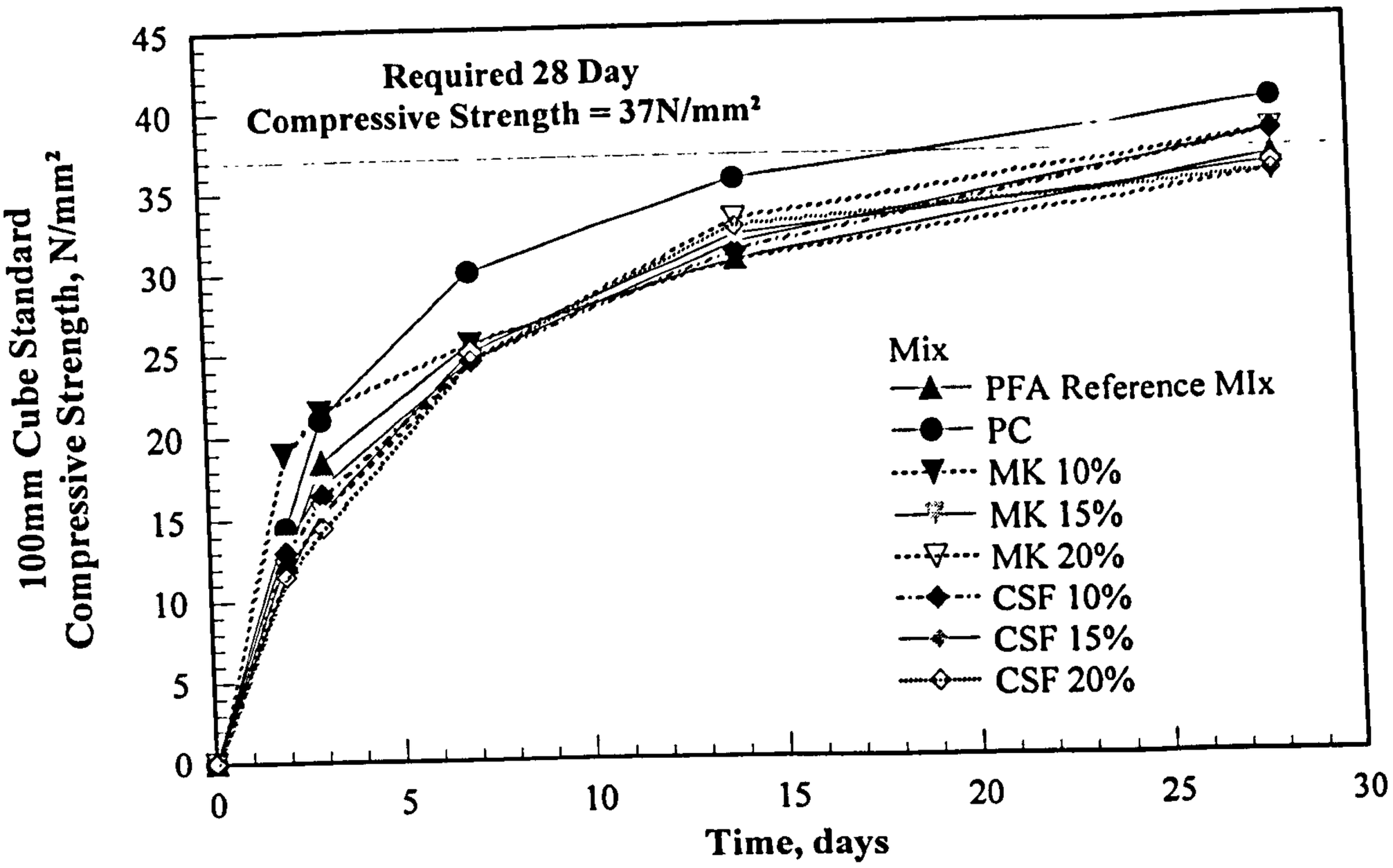


Figure 5.1 Variation in 28 day compressive strength of primary mixes in Series 1.

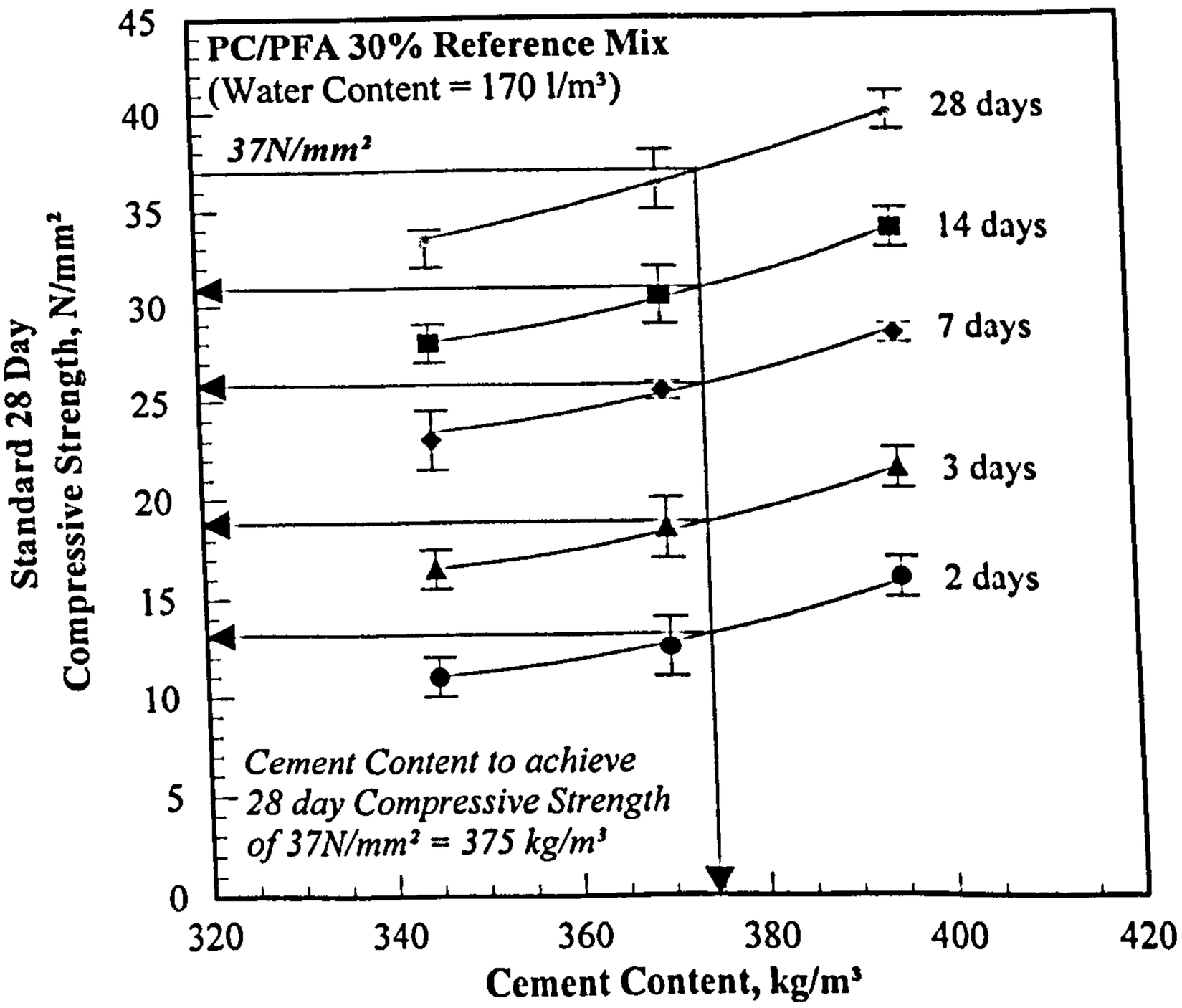


Figure 5.2 Example of adjustment to mix cement content to achieve desired 28 day strength for PC/PFA 30% mix.

Table 5.1 Example of normalisation and adjustment of concrete mix proportions to achieve 28 day compressive strength of 37N/mm².

Mix	Cement Content kg/m³	Test Age, days					2/28 day ratio
		2	3	7	14	*28*	
(a) Mean Compressive Strength Results, N/mm²							
Secondary - 8% Cement	345	11.0	16.5	23.0	28.0	*33.5*	**0.33**
Primary Mix	370	12.5	18.5	25.5	30.5	*36.5*	**0.34**
Secondary +8% Cement	395	16.0	21.0	28.5	34.0	*40.0*	**0.40**

(b) Adjusted Mix Proportions to Achieve 37N/mm²at 28 days, kg/m³

	PC+PFA	Water	Sand	10mm	20mm	w/c ratio
PC/PFA 30%	375	170	640	400	800	0.45

Table 5.2 Comparison of compressive strength from normalised mix proportions using normalisation procedure and compressive strength from actual concrete cast using normalised mix proportions.

PC/PFA 30% Reference Mix	Cement Content kg/m³	Test Age, days					2/28 day ratio
		2	3	7	14	*28*	
Compressive strength using normalisation procedure, N/mm²	375	13.0	19.0	26.0	31.0	*37.0*	**0.35**
Compressive strength from actual concrete mix, N/mm²	375	13.0	18.5	26.0	31.5	*37.0*	**0.35**
Difference (normalised - actual)		±0.0	0.5	±0.0	-0.5	*±0.0*	

Table 5.3 Normalised mix constituent proportions for Reference Mix and Series 1 Test Mixes.

Cement Type	CEM Class[1]	Normalised Mix Constituent Proportions, kg/m³					Plasticiser Dosage, l/100kg Cement	w/c ratio
		Cement Content	Water [2]	Aggregates: Sand [3]	Aggregates: 10 mm [4]	Aggregates: 20 mm [4]		
Reference Mix								
PFA 30%	II/B-V	375	170	640	400	800	none required	0.46
Test Mixes								
Portland Cement								
PC	I	300	185	700	400	800	none required	0.59
Metakaolin								
MK 10%	II/A-Q	315	185	685	400	800	0.55	0.61
MK 15%	II/A-Q	285	185	715	400	800	0.62	0.63
MK 20%	II/A-Q	280	185	720	400	800	0.63	0.64
Silica Fume								
CSF 10%	II/A-D	280	185	720	400	800	0.60	0.66
CSF 15%	II/A-Q	285	185	715	400	800	0.61	0.64
CSF 20%	II/A-Q	290	185	710	400	800	0.63	0.63

[1] Cement designation in BS EN 197-1.

[2] Free water content to achieve slump class S2 to BS EN206 (60-90mm). Plasticizer used as shown.

[3] Natural sand, zone M grading to BS 812:1992.

[4] Coarse aggregate: natural gravel.

With the exception of MK 10%, the MK and all CSF mixes had lower cement contents than the PC mix, on average a reduction of between 10 and 20kg/m^3 of cement. MK and CSF mixes required varying dosages of plasticiser to ensure workability was within slump class S2 of BS EN 206-1. An upper limit of 185l/m^3 free water was used in an attempt to reflect the typical limit used in contemporary structural concrete (Jones et al, 2000).

5.3 COMPRESSIVE STRENGTH DEVELOPMENT OF TEST SERIES 1 MIXES

The modifications made to the CEN test for carbonation in the present study recommended that specimens be subjected to carbonation at a similar strength rather than age. Therefore, an initial curing regime of seal curing specimens until they achieved $0.5f_{cm,28}$ (18.5N/mm^2) was adopted. This followed the curing recommendations as specified in ENV 13670-1: Execution of concrete structures - Part 1: Common rules. A series of 100mm cube specimens were standard cured for each mix to determine the difference between sealed and standard curing on early strength development. This determined at which point the CEN specimens should be transferred to the test chamber.

5.3.1 Standard Cured Compressive Strength Development

Table 5.4 shows the compressive strength development of standard cured 100mm cube specimens up to a period of 1 year (364 days). All mixes were normalised to 37N/mm^2 at 28 days, however it is the early strength development which is of importance in determining the length of curing for the CEN test. The MK 10% mix exhibited a rapid early strength gain up to 7 days, having a 2/28 day ratio of 0.54. Although the reasons for this phenomenon are not entirely clear, the MK 10% had a higher cement content than the PC mix and, indeed, the PC content of the mix, which is the driving force behind early strength gain, was 284kg/m^3. This, coupled with the ultra fine nature of the MK may well have contributed to this rapid early strength gain. A similar phenomenon has been observed by ECC (ECC, 1996). The remaining MK and CSF mixes presented a relatively low early strength gain indicating that, compared to a standard PC mix, a longer curing period may be required prior to CEN storage. The PC/PFA 30% Reference Mix also showed a slower strength gain up to 28 days.

5.3.2 Comparison Between Seal Cured and Standard Cured Specimens

A comparison between the time taken to reach $0.5f_{cm,28}$ for standard curing and sealed curing is shown in Figure 5.3. The PC, MK 15%, MK 20% and all CSF mixes showed that although there were slight differences in early strength development within the standard cured specimens, the differences were reflected in the seal cured specimens and, up to 4 days, the

Table 5.4 Normalised standard cured 100mm cube compressive strength results for Series 1 Test Mixes.

Mix	Cement Content kg/m³	Test Age, days									2/28 day ratio
		2	3	7	14	28	60	90	180	364	
Reference Mix											
PFA	375	11.5	15.5	24.0	31.0	*37.0*	42.5	43.5	46.5	48.5	**0.31**
Series 1 Mixes											
PC	300	13.0	19.0	27.0	32.5	*37.0*	39.5	42.5	44.0	45.0	**0.35**
MK 10%	315	20.0	25.0	27.0	32.0	*37.0*	39.0	41.0	43.5	45.5	**0.54**
MK 15%	285	13.0	16.0	23.5	30.5	*37.0*	39.5	42.5	44.0	44.5	**0.35**
MK 20%	280	10.5	14.0	23.0	31.0	*37.0*	40.0	41.5	42.5	43.0	**0.28**
CSF 10%	280	12.0	15.5	23.0	30.0	*37.0*	40.5	42.5	43.5	44.0	**0.32**
CSF 15%	285	11.0	14.5	22.0	30.0	*37.0*	40.0	42.0	43.5	43.5	**0.30**
CSF 20%	290	11.0	14.0	22.0	30.0	*37.0*	39.5	42.0	43.0	43.5	**0.30**

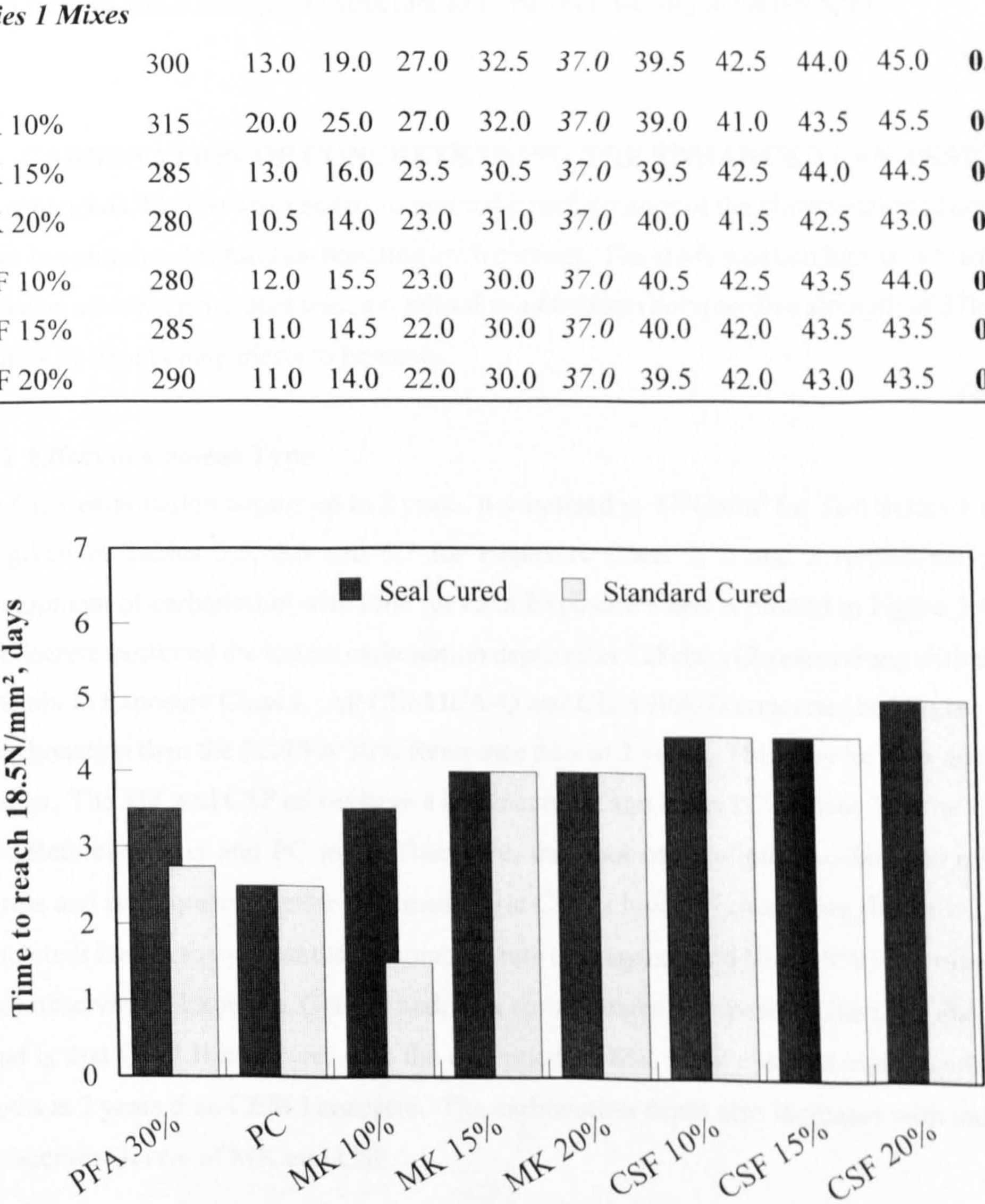


Figure 5.3 Comparison of time to reach 18.5N/mm² for seal cured and standard cured mixes in Test Series 1.

difference in rate of compressive strength development was negligible for seal cured and standard cured specimens. The PC/PFA 30% Reference Mix required an additional day in seal curing to achieve the $0.5f_{cm,28}$. This was attributed to the higher replacement level of PFA within the mix. The MK 10% mix, which had shown a very rapid early strength gain in standard curing, had a similar seal cured strength development to that of the PC/PFA 30% Reference Mix, with $0.5f_{cm,28}$ achieved after 3.5 days. The MK 10% mix appeared to be very sensitive to the curing regime and exposure to moisture, but clearly required the availability of moisture to allow the hydrate structure to form more rapidly at earlier ages.

5.4 CARBONATION OF CONCRETE USING THE ENHANCED CEN TEST

The enhanced CEN test was used to compare the performance of the aforementioned concrete mixes in a simulated natural carbonating environment. The study was conducted over a period of 2 years and data generated was normalised to a common compressive strength of 37N/mm^2 to allow an exact comparison to be made.

5.4.1 Effect of Cement Type

The CEN carbonation depths up to 2 years, normalised to 37N/mm^2 for Test Series 1 mixes, are given in Tables 5.5, 5.6 and 5.7 for Exposure Class 1, 2 and 3 respectively. The development of carbonation with time for each Exposure Class is plotted in Figure 5.4. The PC concrete exhibited the lowest carbonation depth after 728 days (2 years) along with the MK 10% mix in Exposure Class 1. All CEM II/A-Q and CEM II/A-D concretes had higher depths of carbonation than the PC/PFA 30% Reference Mix at 2 years. This may be for a number of reasons. The MK and CSF mixes have a lower cement and lower PC content than the PC/PFA 30% Reference Mix and PC mix. Therefore, the pool of alkalinity available to resist the ingress and subsequent reaction of atmospheric CO_2 is lower. Lower pore fluid alkalinity in concrete is known to increase the carbonation rate (Kobayashi and Uno, 1990). Similar trends were observed in Exposure Class 2 and, to a certain extent, Exposure Class 3. The overall trend is that CEM II concrete, with the exception of MK 10%, exhibits higher carbonation depths at 2 years than CEM I concrete. The carbonation depth also increases with increasing replacement levels of MK and CSF.

Figure 5.5 compares the effect of cement type on the depth of carbonation at 2 years for Test Series 1 mixes. The effects of cement type are more noticeable in Exposure Class 1 with the PC/PFA 30% Reference Mix having a carbonation depth of 5.5mm at 2 years.

Table 5.5 Normalised CEN carbonation depths for Test Series 1 mixes in Exposure Class 1.

Mix	CEM Designation	Depth of Carbonation in CEN Exposure Class 1, mm						
		28 d	91 d	182 d	273 d	364 d	546 d	728 d
PC/PFA 30%	CEM II/B-V	1.0	2.0	3.0	3.5	4.0	4.5	5.5
PC	CEM I	0.5	1.0	1.5	2.0	2.0	2.5	3.0
MK 10%	CEM II/A-Q	0.5	1.0	1.5	1.5	1.5	2.0	3.0
MK 15%	CEM II/A-Q	1.5	3.0	4.0	5.0	5.5	6.0	7.0
MK 20%	CEM II/A-Q	2.0	3.5	4.5	5.5	5.5	6.5	7.5
CSF 10%	CEM II/A-D	2.0	3.0	4.5	5.0	5.5	6.0	6.5
CSF 15%	CEM II/A-Q	2.0	3.5	4.5	5.5	6.0	6.5	7.0
CSF 20%	CEM II/A-Q	2.0	3.5	4.5	5.5	6.5	7.0	7.5

Table 5.6 Normalised CEN carbonation depths for Test Series 1 mixes in Exposure Class 2.

Mix	CEM Designation	Depth of Carbonation in CEN Exposure Class 2, mm						
		28 d	91 d	182 d	273 d	364 d	546 d	728 d
PC/PFA 30%	CEM II/B-V	0.5	1.5	2.0	2.0	2.5	3.0	3.5
PC	CEM I	0.5	0.5	1.0	1.5	1.5	2.0	2.5
MK 10%	CEM II/A-Q	0.5	0.5	1.0	1.0	1.0	1.5	2.0
MK 15%	CEM II/A-Q	1.0	2.5	3.5	3.5	4.0	4.5	5.0
MK 20%	CEM II/A-Q	1.5	3.0	4.0	4.5	5.0	5.5	6.0
CSF 10%	CEM II/A-D	1.0	2.0	2.5	2.5	3.0	3.0	3.5
CSF 15%	CEM II/A-Q	1.5	2.5	3.0	3.5	3.5	4.0	4.5
CSF 20%	CEM II/A-Q	1.5	2.5	3.0	3.5	4.0	4.5	5.0

Table 5.7 Normalised CEN carbonation depths for Test Series 1 mixes in Exposure Class 3.

Mix	CEM Designation	Depth of Carbonation in CEN Exposure Class 3, mm						
		28 d	91 d	182 d	273 d	364 d	546 d	728 d
PC/PFA 30%	CEM II/B-V	0.5	1.0	1.5	1.5	1.5	2.0	2.0
PC	CEM I	0.5	0.5	1.0	1.0	1.5	1.5	2.0
MK 10%	CEM II/A-Q	0.0	0.5	0.5	0.5	1.0	1.5	2.0
MK 15%	CEM II/A-Q	0.5	1.5	2.0	2.0	2.5	2.5	3.0
MK 20%	CEM II/A-Q	0.5	1.5	2.0	2.5	3.0	3.0	3.5
CSF 10%	CEM II/A-D	0.5	1.5	2.0	2.5	2.5	3.0	3.5
CSF 15%	CEM II/A-Q	0.5	1.5	2.0	2.5	3.0	3.0	3.5
CSF 20%	CEM II/A-Q	0.5	1.0	2.0	2.5	2.5	3.0	3.5

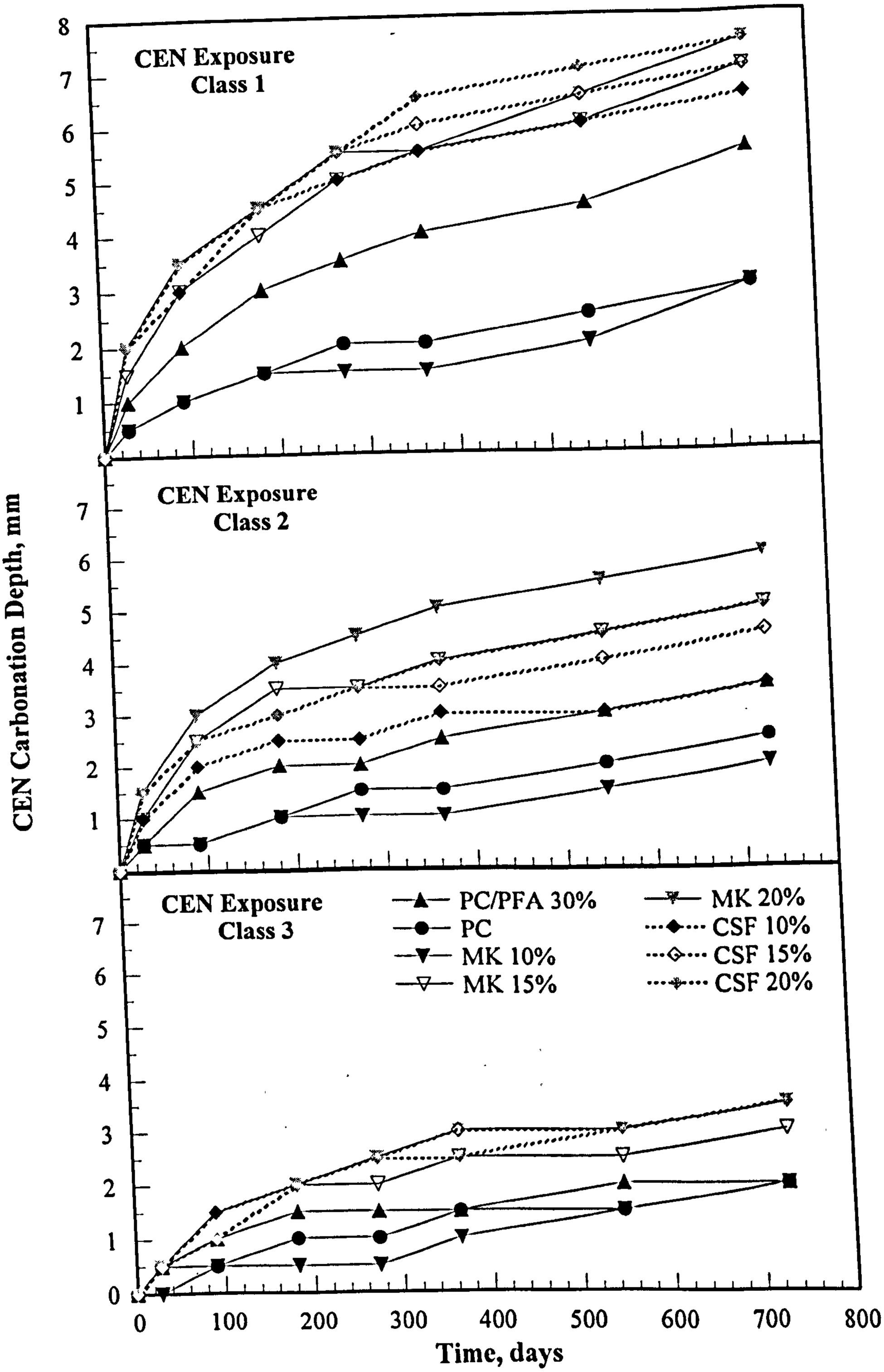


Figure 5.4 Development of CEN carbonation with time for Test Series 1 mixes in Exposure Classes 1, 2 and 3.

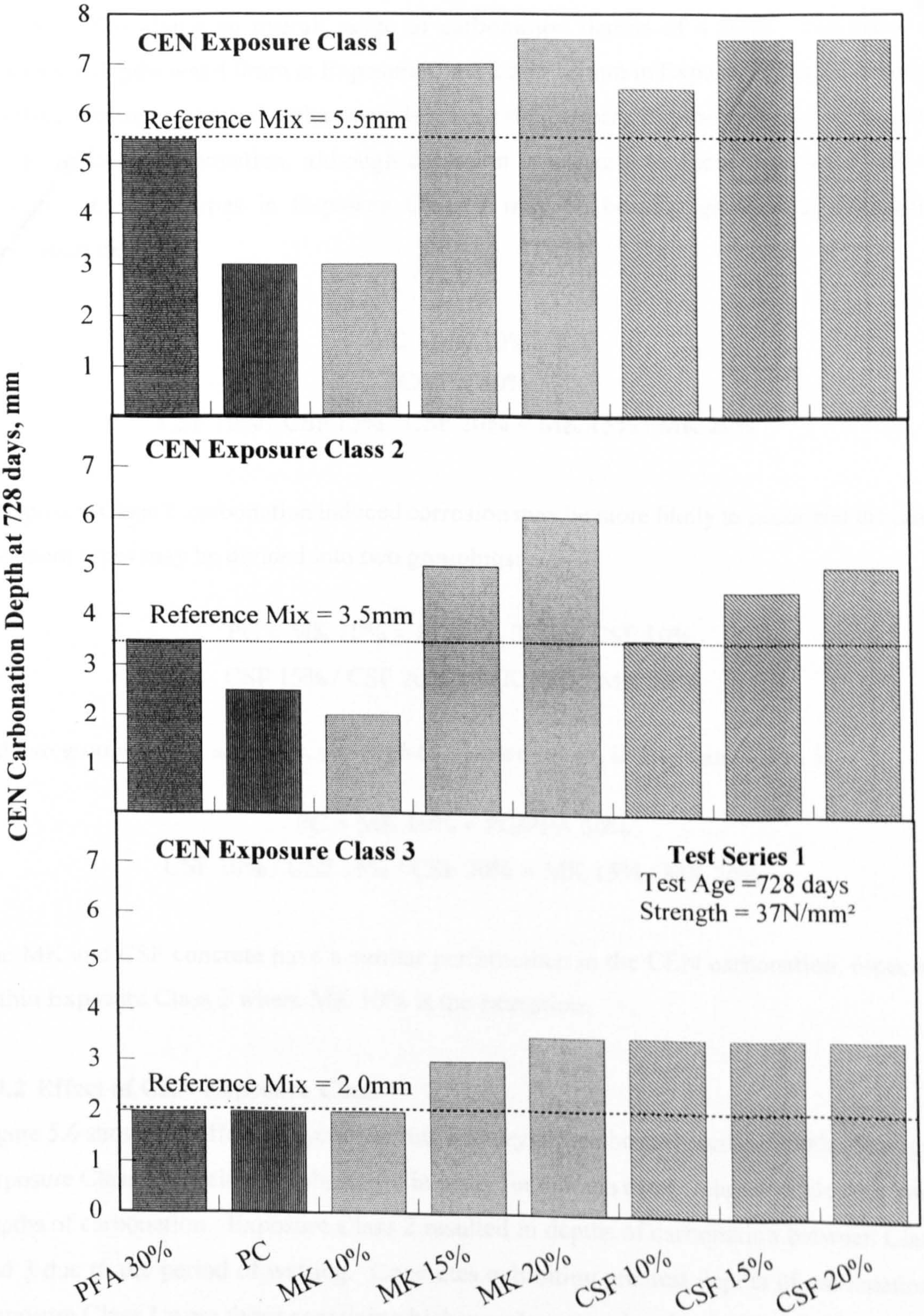


Figure 5.5 Depth of CEN Carbonation specimens normalised to 37N/mm² at 2 years for Series 1 mixes in Exposure Classes 1, 2 and 3.

For, Exposure Class 1, the maximum depth of carbonation was 7.5mm (MK 20%, CSF 15% and CSF 20%) giving an overall range of carbonation depths of 4.5mm. The range of carbonation depths was 4.0mm in Exposure Class 2 and 1.5mm in Exposure Class 3, although the effect of cement type and replacement level can still be seen. Exposure Class 1 is the worst case scenario for carbonation, although corrosion is unlikely to occur due to the lack of moisture. Cement types in Exposure Class 1 may be broadly grouped by increasing carbonation depth as:

PC ≈MK 10%

PC/PFA 30%

CSF 10% / CSF 15% / CSF 20% ≈ MK 15% / MK 20%

In Exposure Class 2, carbonation induced corrosion may be more likely to occur and the range of cement types may be divided into two groupings:

PC ≈ MK 10% ≈ PC/PFA 30% ≈ CSF 10%

CSF 15% / CSF 20% ≈ MK 15% / MK 20%

and two groupings are apparent, although to a lesser extent, in Exposure Class 3:

PC ≈ MK 10% ≈ PC/PFA 30%

CSF 10% / CSF 15% / CSF 20% ≈ MK 15% / MK 20%

The MK and CSF concrete have a similar performance in the CEN carbonation, especially within Exposure Class 3 where MK 10% is the exception.

5.4.2 Effect of CEN Exposure Class

Figure 5.6 shows the effect of cyclic wetting and drying on the carbonation depth. Storage in Exposure Class 3 (specimens submerged in water for 6 hours every 7 days) yielded the lowest depths of carbonation. Exposure Class 2 resulted in depths of carbonation between Class 1 and 3 due to the period of wetting. Concretes exhibiting greatest depths of carbonation in Exposure Class 1 were those containing higher replacement levels of MK and CSF and, to a lesser extent, the PC/PFA 30% Reference Mix. These were more sensitive to increasing exposure to moisture, particularly in Exposure Class 3. The PC/PFA 30% Reference mix showed a 63% reduction in carbonation depth from Exposure Class 1 and 3, whereas MK 20%

and CSF 20% mixes showed carbonation depths reduced by 55% when specimens were wetted every 7 days.

Increasing exposure to moisture will inhibit the ingress of CO_2 and suppress the carbonation reaction in two ways:

(i) Increasing pore saturation levels will physically inhibit CO_2 ingress and therefore reduce the rate at which the subsequent carbonation chemical reactions occur (Parrott, 1991).

(ii) Hydration reactions in the outer layer of the concrete may be initiated again due to the presence of moisture, leading to a refined microstructure. This depends on the length of saturation, depth of moisture penetration and initial degree of hydration.

The reduction in carbonation depths between Exposure Class 1 and 3 may be due to a combination of these phenomena. Appendix B shows the CEN carbonation specimens at 1 year for all three Exposure Classes. In all cases, the effect of increasing the wetting/drying cycles can be clearly seen, with the carbonation depth reduced on all faces of the specimens.

The provision of Exposure Classes in the CEN test was in attempt to provide a comparison between simulated natural exposure and real exposure conditions. A comparison between the effect of CEN Exposure Class and actual exposure under UK climate conditions is discussed in Chapter 7.

5.4.3 Relative Ranking of Cement Types and Test Stability

The relative ranking of cement types was examined over the test period with respect to the PC/PFA 30% Reference Mix. As the CEN test was identified as having the potential to be developed for use as a performance specification, the ability of the test to reliably benchmark unknown performance against a concrete of known performance was vital (Harrison, 1995). In Exposure Class 1, which was deemed to be the worst case scenario for carbonation, relative ranking of the various cement types changed up to a period of18 months (546 days), Figure 5.7. Beyond this, the ranking of carbonation depths did not appear to change. The exceptions were the PC and MK 10% mixes. However, the changes in carbonation depth were relatively small (<0.5mm) and were thus deemed negligible.

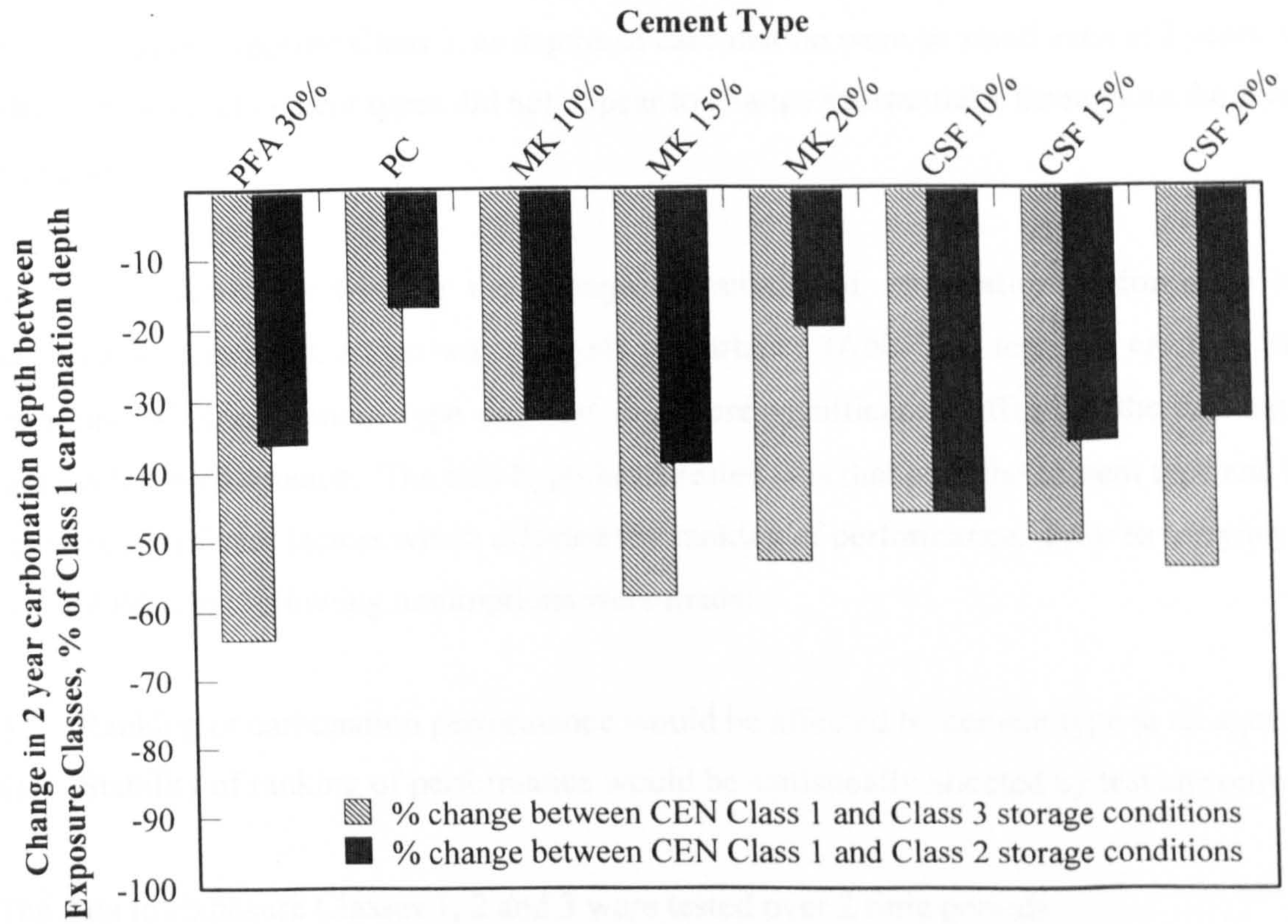


Figure 5.6 Comparison of reduction in CEN carbonation depth at 2 years from Exposure Class 1 to Exposure Classes 2 and 3.

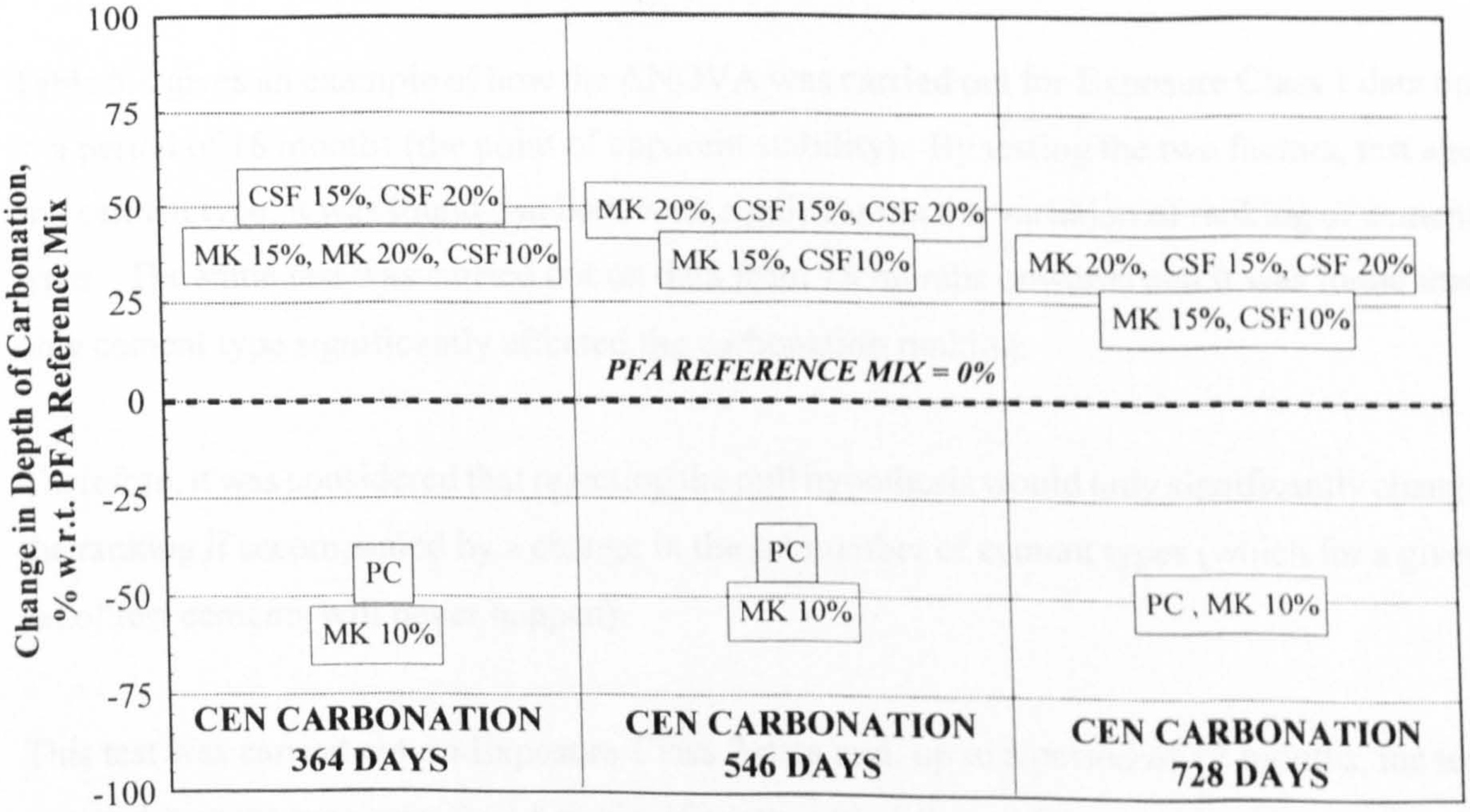


Figure 5.7 Change in relative ranking with time of CEN Class 1 Exposure specimens in Test Series 1 with respect to the PC/PFA 30% Reference Mix.

In Exposure Class 2 the relative ranking of cement types did not change after a period of 364 days and in Exposure Class 3, as depths of carbonation were so small even at 2 years, the relative ranking of cement types did not appear to change substantially throughout the 2 year test period.

In order to determine whether the change in ranking of carbonation performance was statistically significant, a two way analysis of variance (ANOVA) test was carried out to determine whether cement type and test age were significantly affecting the ranking of carbonation performance. The null hypothesis tested was that both the cement type and test age were significant factors which affected the ranking of performance. Prior to carrying out the ANOVA, the following assumptions were made:

i) Ranking of carbonation performance would be affected by cement type at all ages.
ii) Stability of ranking of performance would be statistically affected by test age only.

The data in Exposure Classes 1, 2 and 3 were tested over 2 time periods

i) Up to and including the point of apparent stability;
ii) After the point of apparent stability.

Table 5.8 gives an example of how the ANOVA was carried out for Exposure Class 1 data up to a period of 18 months (the point of apparent stability). By testing the two factors, test age and cement type, it was found that both were significant in the variation of ranking of cement types. The same test was carried out on data from 18 months onwards and it was found that only cement type significantly affected the carbonation ranking.

Therefore, it was considered that rejecting the null hypothesis would only significantly change the ranking if accompanied by a change in the set number of cement types (which for a given set of test cements will never happen).

This test was carried out on Exposure Class 2 data and, up to a period of 12 months, the test age and cement type was found to significantly affect the performance ranking. After 12 months, only cement type had significant influence, indicating that the test method may be carried out up to a period of 12 months in Exposure Class 2.

Table 5.8 2 way ANOVA test to determine whether cement type and test age are significant factors in changing ranking of carbonation performance.

Stage 1 - Ranking of Carbonation Performance*

		Cement Type									
		C_1 PFA 30%	C_2 PC	C_3 MK10%	C_4 MK15%	C_5 MK20%	C_6 CSF10%	C_7 CSF15%	C_8 CSF20%	Σx_1	x_1^2
Test Age	3m	3	1	2	4	8	5	6	7	36	*1296*
	6m	3	1	2	4	8	6	5	7	36	*1296*
	9m	3	2	1	5	8	4	6	7	36	*1296*
	12m	3	2	1	4	6	5	7	8	36	*1296*
	18m	3	1	2	4	8	5	6	7	36	*1296*
	Σx_2	15	7	8	21	38	25	30	36	**180**	*6480*
	x_2^2	*225*	*49*	*64*	*441*	*1444*	*625*	*900*	*1296*	*5044*	

Stage 2 - Analysis of Data

Source of Variation	*Degrees of Freedom*	$SS = \Sigma x^2 - \frac{(\Sigma x)^2}{n}$	$Mean\ Square = \frac{SS}{d.o.f.}$	*F*
Factor 1 Test Age	5 - 1 = 4	$6480/8 - 180^2/40 = <0.01$	<0.01	<0.01
Factor 2 Cement Type	8 - 1 = 7	$5044/5 - 180^2/40 = 198.8$	198.8/7 = 28.4	1.91
Residuals	39 - 4 - 7 = 28	615 - 198.8 - 0.0= 416.2	416.2/28 = 14.9	-
Totals	40 - 1 = 39	$1425 - 180^2/40 = 615$	-	-

Null hypothesis H_0: The cement type and test age are significant in the variation in ranking of carbonation performance

$F_{7, 28} = 2.352$ at a 95% confidence limit (Kennedy and Neville, 1976)

Factor 1, $F < 2.352$ thus we can accept H_0

Factor 2, $F < 2.352$ thus we can accept H_0

Up to a test age of 18 months, both cement type and test age are significant in the variation of the ranking of carbonation performance

* Ranking from lowest depth to highest depth, ie: 1 = lowest, 8 = highest

The carbonation depths obtained from the CEN test programme were analysed to ascertain whether statistical distributions within both a prism grouping and cement type were normal. A normal distribution curve was fitted to the data and the difference between the fitted normal distribution curve (expected frequency) and the actual data (observed frequency) then tested for 'goodness of fit' using a Chi-squared (χ^2) test to a 95% confidence level. An example of this is provided in Appendix B. The data was found to be normally distributed within both single prism sets and combinations of two prisms.

5.5 PERMEATION PROPERTIES OF CEN TEST SPECIMENS UP TO 2 YEARS

Four permeation tests were carried out on concrete stored under CEN test conditions. Tests were carried out at four ages: pre-entry (after removal from the seal curing regime and prior to CEN exposure), 6 months, 1 year, and 2 years.

5.5.1 Initial Surface Absorption Test at 10 Minutes (ISAT-10)

The ISAT-10 results for Test Series 1 mixes are shown in Figure 5.8 (a), (b) and (c) for Exposure Classes 1, 2 and 3 respectively. In all cases the concretes exhibited a reduction in ISAT-10 with time. The PC and PC/PFA 30% Reference Mix showed the highest ISAT-10 at pre-entry with the CEM II concrete having lower ISAT-10 values. The MK 10% had the lowest ISAT-10 at pre-entry which was expected due to the rapid early strength gain. The ISAT-10 of the MK 10% concrete did not exhibit as great a reduction compared to the other concretes . The reduction in ISAT-10 with time may be due to a number of factors including continuing hydration and the effects of the carbonation mechanism at the concrete surface (Hilsdorf et al, 1984). A greater reduction in ISAT-10 with time was observed in Exposure Classes 2 and 3, increasing with the availability of moisture, although the relative ranking of ISAT-10 was very similar in all Exposure Classes at all test ages.

5.5.2 Intrinsic Air Permeability

The changes in Intrinsic Air Permeability with time for concretes exposed in the CEN test chamber are shown in Figure 5.8 (d), (e) and (f). The PC/PFA 30% Reference Mix and PC mixes exhibit a distinctly higher intrinsic air permeability than the CEM II concretes at all test ages and Exposure Classes. The MK and CSF mixes had a similar intrinsic air permeability at pre-entry, the range of values being 17 - 24 $m^2 \times 10^{-17}$.

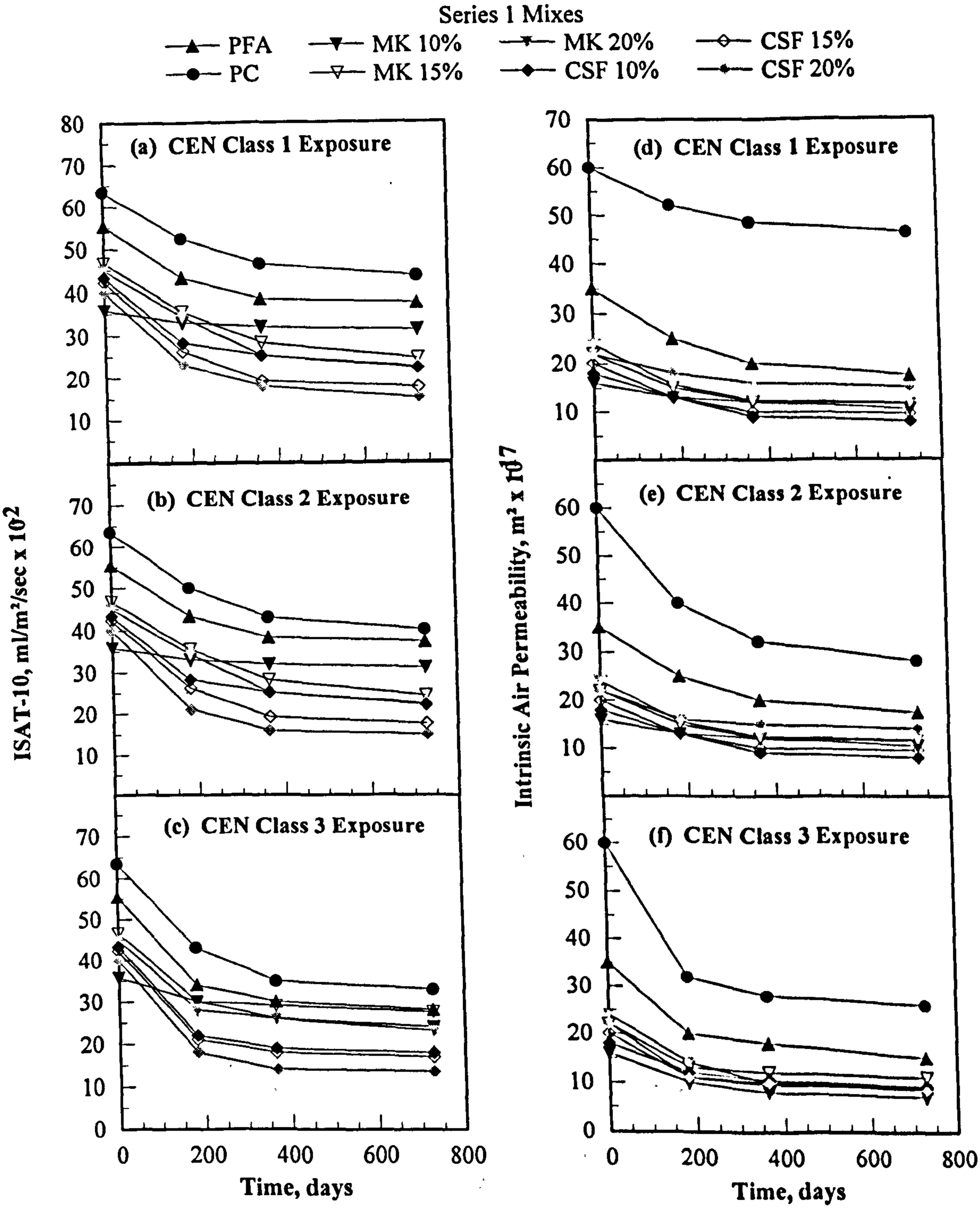


Figure 5.8 Change in ISAT-10 for Series 1 mixes in CEN Exposure (a) Class1, (b) Class 2, (c) Class 3 and change in Intrinsic Air Permeability of Series 1 mixes in CEN Exposure (d) Class 1, (e) Class 2, (f) Class 3. *Time 0 is measurement prior to exposure in CEN Test Chamber.*

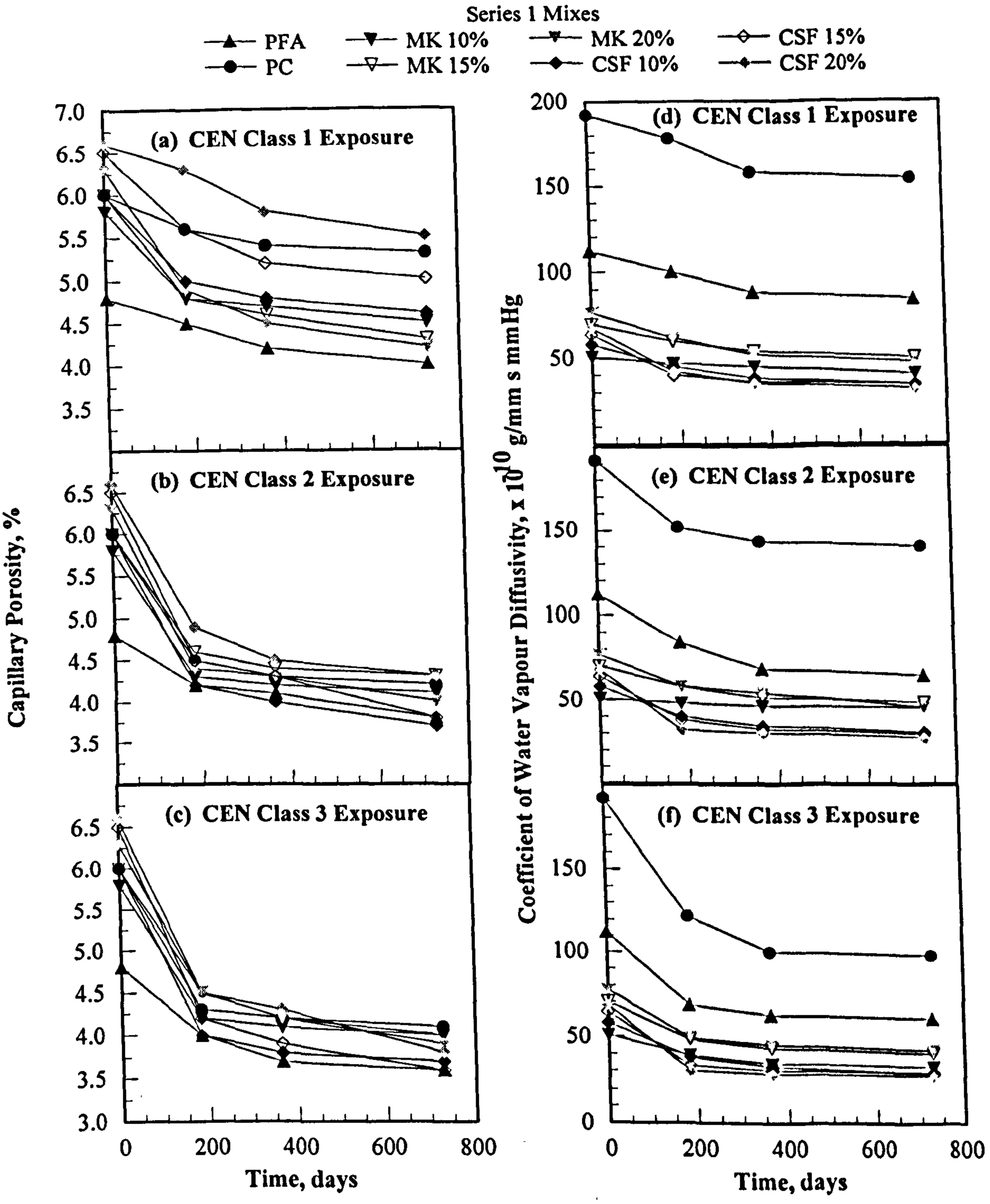


Figure 5.9 Change in Capillary Porosity for Series 1 mixes in CEN Exposure (a) Class1, (b) Class 2, (c) Class 3 and change in Water Vapour Diffusivity of Series 1 mixes in CEN Exposure (d) Class 1, (e) Class 2, (f) Class 3. *Time 0 is measurement prior to exposure in CEN Test Chamber.*

Again, the availability of moisture from Exposure Classes 2 and 3 led to a greater reduction in intrinsic air permeability with time. This was most noticeable in the PC mix with a reduction of 30 $m^2 x10^{-17}$ in Exposure Class 3 compared to 12 $m^2 x 10^{-17}$ in Exposure Class 1. The trends were similar between ISAT-10 and intrinsic air permeability even though they measured quite different properties of the concrete.

5.5.3 Capillary Porosity

The change in capillary porosity with time and exposure to moisture is shown in Figure 5.9 (a), (b) and (c) for CEN Exposure Classes 1, 2 and 3 respectively. Across all Exposure Classes, the trend indicated a reduction in capillary porosity with time, although the reduction is more noticeable with increasing moisture availability. It is interesting to note that the relative ranking of capillary porosity is very different than ISAT or intrinsic air permeability with CSF 20% having the highest capillary porosity in Class 1 Exposure. The PC/PFA 30% Reference Mix actually had the lowest capillary porosity although the remaining CEM II concrete had relatively similar capillary porosities.

5.5.4 Water Vapour Diffusivity (WVD)

The changes in WVD of the outer 25mm of Test Series 1 mixes in the CEN test chamber are shown in Figure 5.9 (d), (e) and (f). The trends are very similar to that in ISAT and intrinsic air permeability with PC mix having the highest WVD followed by the PC/PFA 30% Reference Mix. All CEM II concretes had a relatively similar WVD, with the range of WVD across MK and CSF mixes being reduced with increasing availability of moisture. Table 5.9 compares the WVD for the outer 25mm of concrete with the inner 25mm concrete in Exposure Class 1 and illustrates how the WVD is, in all cases, greater in the 25mm cover concrete than in the internal concrete.

5.5.5 Repeatability of Permeation Tests

A repeatability study of the four permeation tests used was carried out by casting 10 PC/PFA 30% Reference Mix concretes. Table 5.10 gives the results of the tests and the statistical analysis of the repeatability study. The WVD test had the lowest coefficient of variation, V, with 4.0%. ISAT-10 and intrinsic air permeability had coefficients of variation of 5.0% and 5.9% respectively, which was still felt to be acceptable. However, the capillary porosity test was found to be the most variable with a coefficient of variation of 8.6% and was deemed unsuitable for further use in the study.

Table 5.9 Comparison of Water Vapour Diffusivity of surface 0-25mm and 25-50mm of Series 1 mixes in Exposure Class 1.

Mix	Cement Content kg/m³	Coefficient of Water Vapour Diffusivity, x 10^{-10} g/mm s mm Hg							
		0-25 mm of cover concrete				*25-50mm of cover concrete*			
		Pre-entry	182d	364d	728d	Pre-entry	182d	364d	728d
PC/PFA30%	375	112.0	100.0	88.0	84.0	106.0	76.0	48.0	47.2
PC	300	192.0	178.3	158.0	154.1	186.2	135.0	120.0	115.9
MK 10%	315	51.0	47.0	45.0	40.5	49.5	30.0	23.0	20.9
MK 15%	285	70.0	60.0	54.0	50.2	68.6	50.0	41.5	38.6
MK 20%	280	77.0	62.0	52.0	47.4	74.7	60.5	51.3	50.4
CSF 10%	280	58.0	45.0	38.0	34.2	55.7	42.0	35.0	34.0
CSF 15%	285	64.0	40.0	36.0	34.6	62.1	52.9	44.2	42.1
CSF 20%	290	66.0	42.5	35.0	34.0	75.5	58.5	49.3	45.5

Table 5.10 Repeatability results of permeation tests performed on PC/PFA30% concrete seal-cured until $0.5f_{cm,28}$.

Mix	ISA-10, ml/m²/s x 10^{-2}	Water Vapour Diffusivity, x 10^{-10} g/mm s mm Hg	Intrinsic Air Permeability, m²x10^{-17}	Capillary Porosity, %
1	55.2	110.0	36.5	4.1
2	53.5	118.0	37.0	4.5
3	50.6	108.3	37.6	4.6
4	59.9	108.5	37.1	4.9
5	59.5	112.5	35.2	4.2
6	54.5	115.9	40.1	4.0
7	55.6	110.0	42.0	4.8
8	55.5	103.5	38.2	4.6
9	55.0	105.5	35.5	5.1
10	56.0	108.6	35.6	4.8
Mean	**55.5**	**110.1**	**37.4**	**4.6**
Maximum	**59.9**	**118.0**	**42.0**	**5.1**
Minimum	**50.6**	**103.5**	**35.2**	**4.0**
S.D.	**2.5**	**4.2**	**2.1**	**0.3**
***V*[1], %**	***5.0***	***4.0***	***5.9***	***8.6***

[1] V = coefficient of variation (S.D divided by mean)

5.6 ANALYSIS OF SPECIMEN WEIGHT CHANGE

5.6.1 Exposure Class 1

Specimens subjected to Exposure Class 1 conditions were weighed periodically to ascertain any changes in weight due to the formation of products of carbonation. In all cases, there was a rapid weight loss on initial exposure to the CEN environment, attributable to moisture loss, although all specimens showed a slight weight gain after approximately 6 months exposure. This was attributed to the fact that the products of carbonation have a greater mass than the initial hydration products (Parrott, 1991). However, from the current study it is inconclusive whether carbonation can be predicted from weight gain alone as no correlation was found between weight increase and depth of carbonation.

5.6.2 Exposure Classes 2 and 3

The change in weight of prisms in Exposure Classes 2 and 3 was monitored to observe the effects of cyclic wetting and drying. In all cases, it was observed that between the end of the wetting period and beginning of the next wetting/drying cycle, specimens did not return to their original weight, indicating that some moisture was being held within the near surface pore structure due to a combination of:

(i) Physical retention through hysteresis (Abbas, 2000). Water entrapped within larger pores cannot escape through smaller pores as they are already saturated or semi-saturated (Papadakis et al, 1989);

(ii) Chemically bound through re-initiation of hydration of unhydrated cement particles within the near surface cover zone.

Table 5.11 shows the cumulative weight increase in specimens subjected to cyclic wetting and drying. In all cases, the specimen weight increased over the 2 year test period, with the mass increase being greater in test specimens subjected to more frequent wetting and drying cycles. The depth of moisture penetration during the wetting phase in Classes 2 and 3 was measured by means of a moisture sensitive dye, duramine green. Table 5.12 shows that the depth of penetration decreased with time in all cases, indicating that moisture retention is more likely to be due to chemical interaction rather than hysteresis.

Figure 5.10 shows the relationship between measured 6 hour water absorption at 7 days and the 2 year depth of carbonation. In Exposure Class 1, a reasonable correlation is formed and

Table 5.11 Cumulative weight increase of CEN carbonation specimens in Exposure Classes 2 and 3 at 28 days, 6 months and 1 year.

Cement Type	Cumulative Weight Increase[1], % by Weight of Concrete at Exposure to Carbonation					
	Exposure Class 2			Exposure Class 3		
	28 days	1 Year	2 Years	28 days	1 Year	2 Years
PC/PFA30%	2.40	2.85	3.10	2.50	2.90	3.15
PC	2.10	2.60	2.85	3.50	3.90	4.10
MK 10%	2.65	3.05	3.35	3.00	3.80	4.20
MK 15%	2.50	2.85	3.00	3.10	3.90	4.40
MK 20%	2.20	2.75	3.00	3.20	3.60	4.00
CSF 10%	2.10	2.40	2.55	2.50	3.20	3.75
CSF 15%	2.20	2.40	2.60	2.60	3.25	3.85
CSF 20%	2.25	2.45	2.65	2.70	3.45	3.90

[1] Weight change measured to nearest 0.1g and rounded to nearest 0.5g

Table 5.12 Penetration of moisture measured after 6 hours on CEN Exposure Class 2 and Class 3 specimens.

Cement Type	Depth of Moisture Penetration After 6 Hours Absorption, mm					
	Exposure Class 2			Exposure Class 3		
	28 days	1 year	2 years	28 days	1 year	2 years
PC/PFA 30%	8.5	5.5	3.0	5.0	4.0	2.0
PC	6.5	5.5	3.0	3.0	2.5	2.0
MK 10%	6.5	5.0	4.0	4.5	3.5	3.0
MK 15%	10.0	7.5	5.0	7.0	5.0	4.5
MK 20%	11.5	8.5	6.5	8.5	6.0	5.5
CSF 10%	10.0	7.5	5.5	6.5	5.5	5.0
CSF 15%	11.5	7.0	6.0	7.0	6.0	5.5
CSF 20%	11.5	7.5	6.5	7.5	6.5	6.0

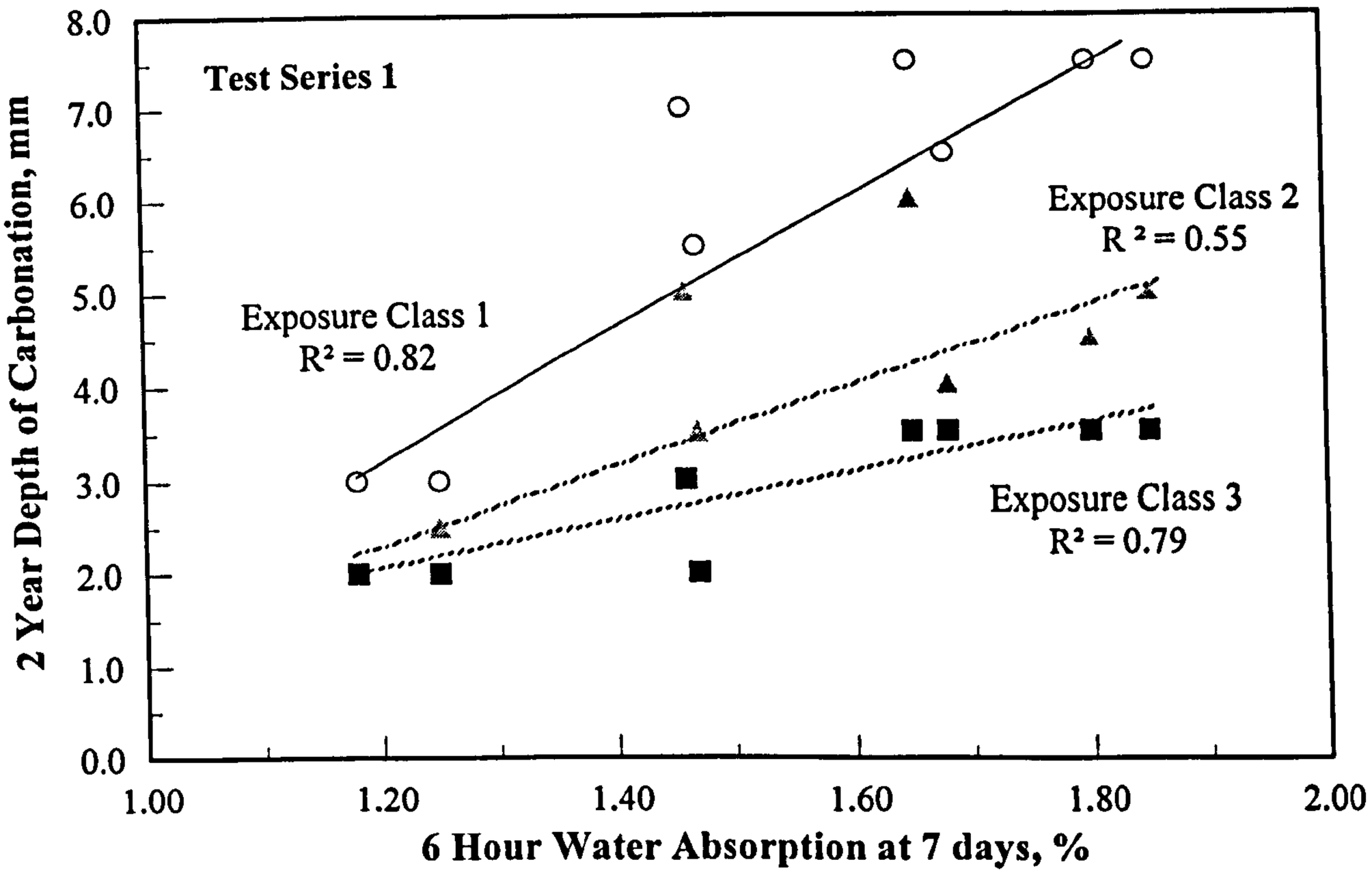


Figure 5.10 Relationship between 6 hour water absorption after 7 days and 2 year depth of carbonation for Test Series 1 mixes.

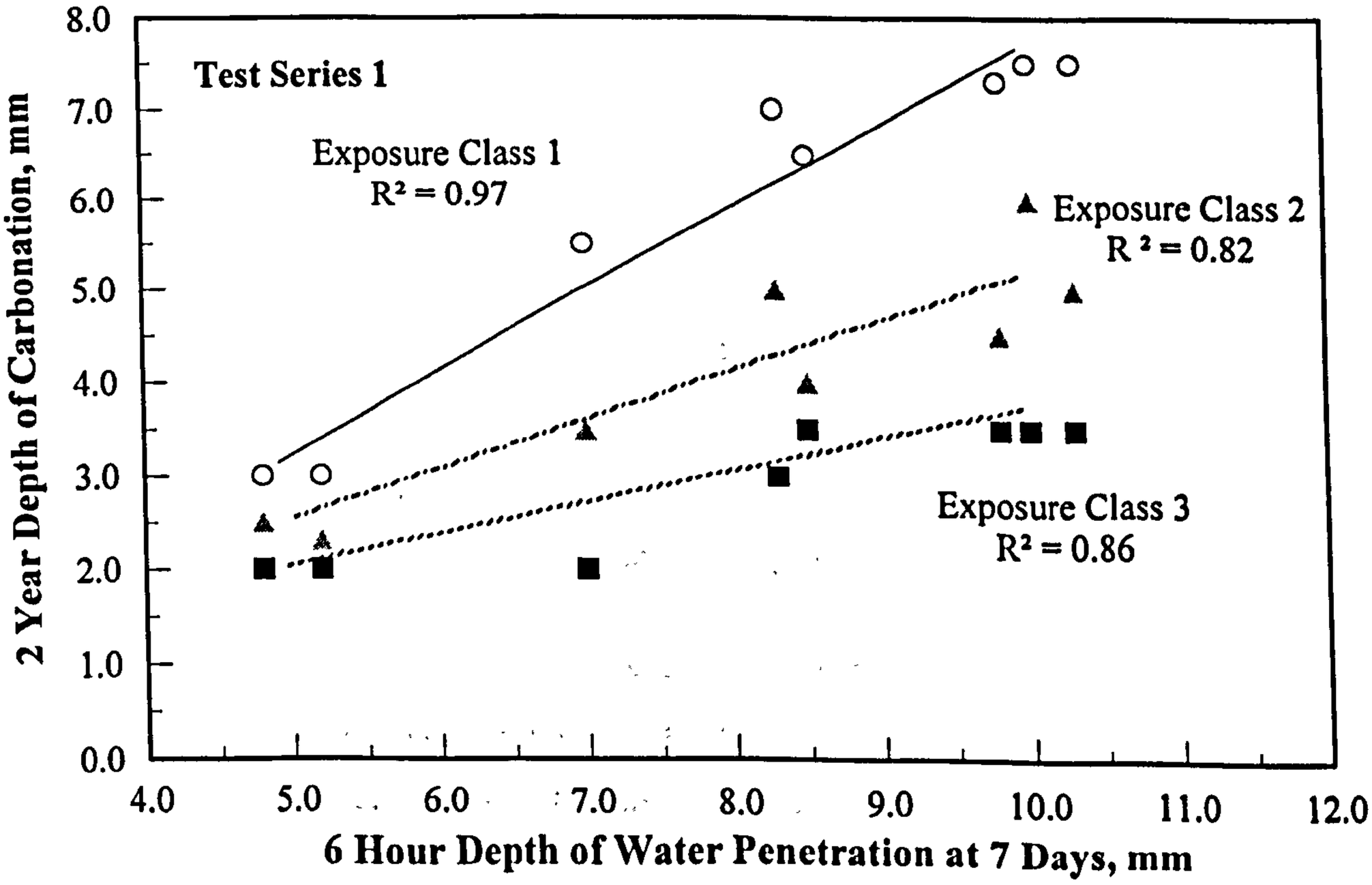


Figure 5.11 Relationship between depth of water penetration after 6 hours at 7 days and 2 year depth of carbonation for Test Series 1 mixes.

predicting carbonation performance may be possible by absorption, as other research has concluded (Parrott, 1991). However, in Exposure Classes 2 and 3, the effects of continued exposure to moisture on the cover concrete properties vary for different cement types, leading to a variation in performance compared to Exposure Class 1. Figure 5.11 provides a better correlation between the penetration depth of moisture at early ages and carbonation at 2 years. This indicates that the physical near surface properties of CEM II concretes are playing a major role in the resistance of carbonation.

5.7 HYDRATION STUDY

The outer layer of concrete is the first line of resistance to the ingress and subsequent chemical reaction of CO_2. The hydration characteristics of the cover concrete play a major role in determining the near surface physical and chemical quality.

5.7.1 Degree of Hydration

The degree of hydration within the outer 10mm of the specimens in test Series 1 was examined at profiled depths using thermogravimetric analysis (TG) to observe the effects of the cyclic wetting and drying of Exposure Classes 2 and 3.

The mean degree of hydration over the initial 10mm is summarised in Table 5.13. In all cases, the degree of hydration increased with increasing exposure to moisture at all ages, indicating that the cyclic presence of moisture within the near surface concrete was promoting increased hydration. The CEM I mix had the highest degree of hydration prior to exposure compared to CEM II mixes, and this was more noticeable with MK and CSF mixes. This was attributed to the fact that, although the presence of CSF and MK has been known to improve the hydration characteristics even at early ages (Larbi and Bijen, 1990; Roy et al, 1992), the mixes were designed on an equal 28 day strength basis. Hence, the mixes have a lower cementitious content, higher water cement ratio and, consequently, slower early strength gain.

It is difficult to ascertain the true effect of cyclic wetting and drying on the degree of hydration as measurement by TG depends primarily on the production of $Ca(OH)_2$. This can be affected by a number of factors depending on the mix constituents:

i) $Ca(OH)_2$ produced by the hydration reaction between water and Portland cement;
ii) $Ca(OH)_2$ consumed by chemical reaction with pozzolanic materials in the mix;
iii) $Ca(OH)_2$ consumed by chemical reaction through carbonation;

Table 5.13 Mean degree of hydration over initial 10mm of cover concrete, Test Series 1.

	Mean Degree of Hydration over 10mm Cover Depth, %						
		Exposure Class 1		Exposure Class 2		Exposure Class 3	
	Pre- Entry	1 Year	2 Years	1 Year	2 Years	1 Year	2 Year
PC/PFA 30%	59	64	69	68	71	76	85
PC	69	72	74	73	74	82	83
MK 10%	55	66	68	72	74	79	85
MK 15%	49	60	64	71	74	76	81
MK 20%	48	58	63	72	74	74	85
CSF 10%	54	65	66	73	74	67	81
CSF 15%	51	62	64	73	75	81	85
CSF 20%	54	65	66	73	74	77	81

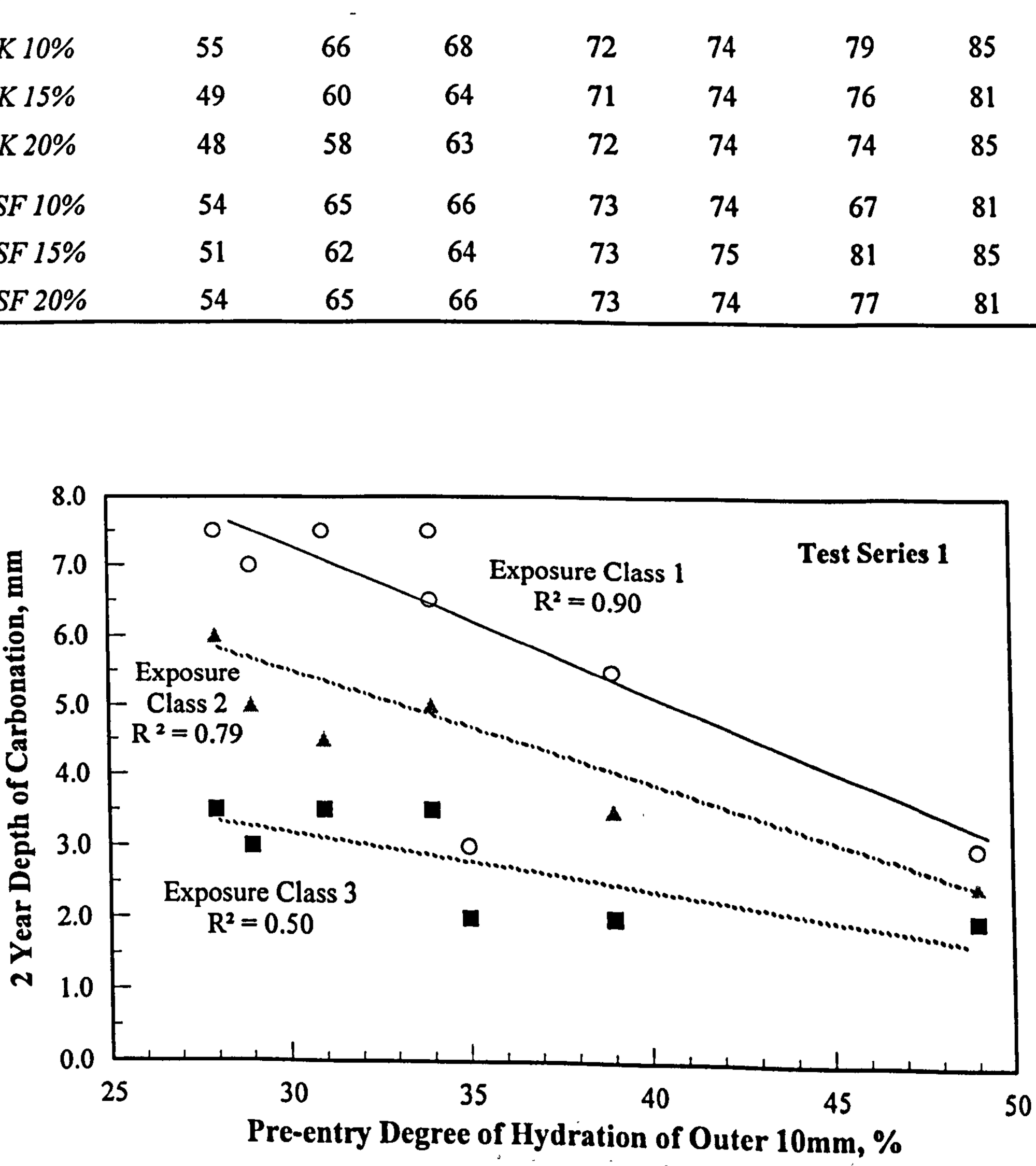


Figure 5.12 Relationship between pre-entry degree of hydration of outer 10mm of specimens and 2 year depth of carbonation for Exposure Classes 1, 2 and 3.

The longer term degree of hydration results will be affected by ii) and iii). It is widely accepted that pozzolanic reactions primarily occur until after 28 days and, at these early ages, levels of carbonation are relatively low. Pre-entry degree of hydration, however, is likely to be mainly governed by i). Figure 5.12 shows that degree of hydration measured at the pre-entry stage has a reasonably good correlation with the two year depths of carbonation in Exposure Class 1. However, this correlation reduces with increasing exposure to moisture.

5.7.2 Total Calcium Hydroxide Content

The total calcium hydroxide content was measured and expressed as a percentage weight of the total 10mm concrete cover to assess the difference in alkalinity within the cover zone. The associated difficulties in measuring the alkalinity of extracted pore fluids meant that analysis by TG was deemed sufficient for the purposes of assessing the available $Ca(OH)_2$ within the cementitious matrix to react with the ingressing CO_2.

Figure 5.13 shows an example of how the total $Ca(OH)_2$ content varied within the outer 10mm of both the PC/PFA30% Reference Mix and PC mix in CEN Exposure Classes 1, 2 and 3. A sharp increase in the total $Ca(OH)_2$ content over the first 10mm of cover was noted, especially in the PC mix. When comparing the region of this sharp increase with the measured depth of carbonation by phenolphthalein, a reasonably good correlation was found, indicating that the carbonation front or, more correctly, neutralisation front was confirmed by TG analysis.

Figure 5.14 shows an example of how the $Ca(OH)_2$ content varied compared with the phenolphthalein measurement for the PC concrete at 1 year, confirming that the neutralisation effect was governed by the amount of total calcium hydroxide within the cover zone. Similar effects were also found in the PFA, MK and CSF mixes, however, the effect of a reduction in $Ca(OH)_2$ due to carbonation was less noticeable as the pozzolanic reaction was also consuming $Ca(OH)_2$ during the test period.

Table 5.14 compares the total $Ca(OH)_2$ within the 10mm cover zone prior to and after the two year test period for mixes in Test Series 1. The mixes are ranked in order of reducing total cover $Ca(OH)_2$ at pre-entry stage. Mixes having a higher initial $Ca(OH)_2$ content, ie: PC and MK 10% exhibited the lowest carbonation depths at 2 years and, indeed, the relative ranking of the cement types was similar to that as per the depth of carbonation at 2 years.

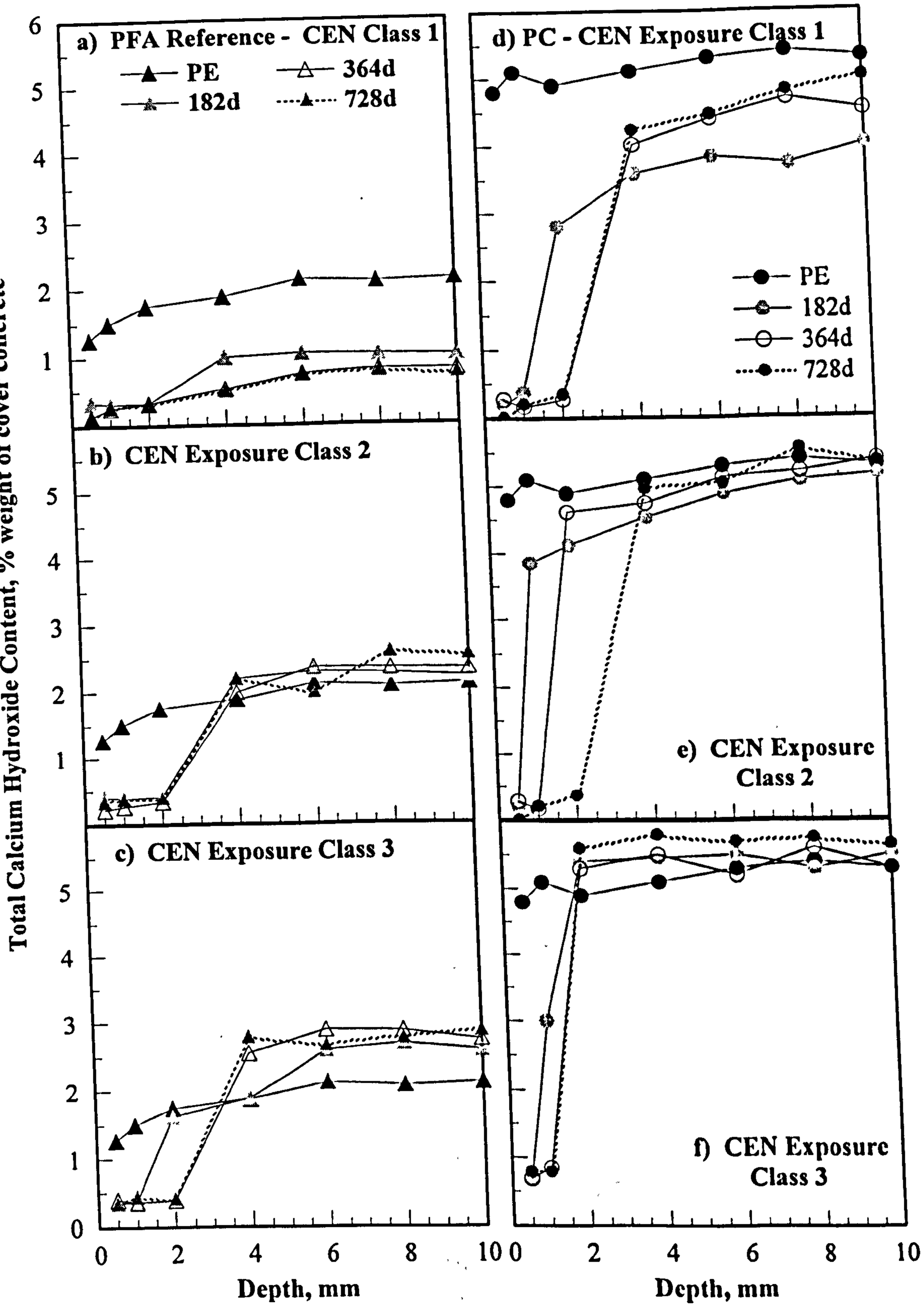


Figure 5.13 Total calcium hydroxide ($Ca(OH)_2$) profiles for PFA Reference (a, b, c) and PC (d, e, f) mixes showing the change in levels of $Ca(OH)_2$ within the 10mm concrete cover zone.

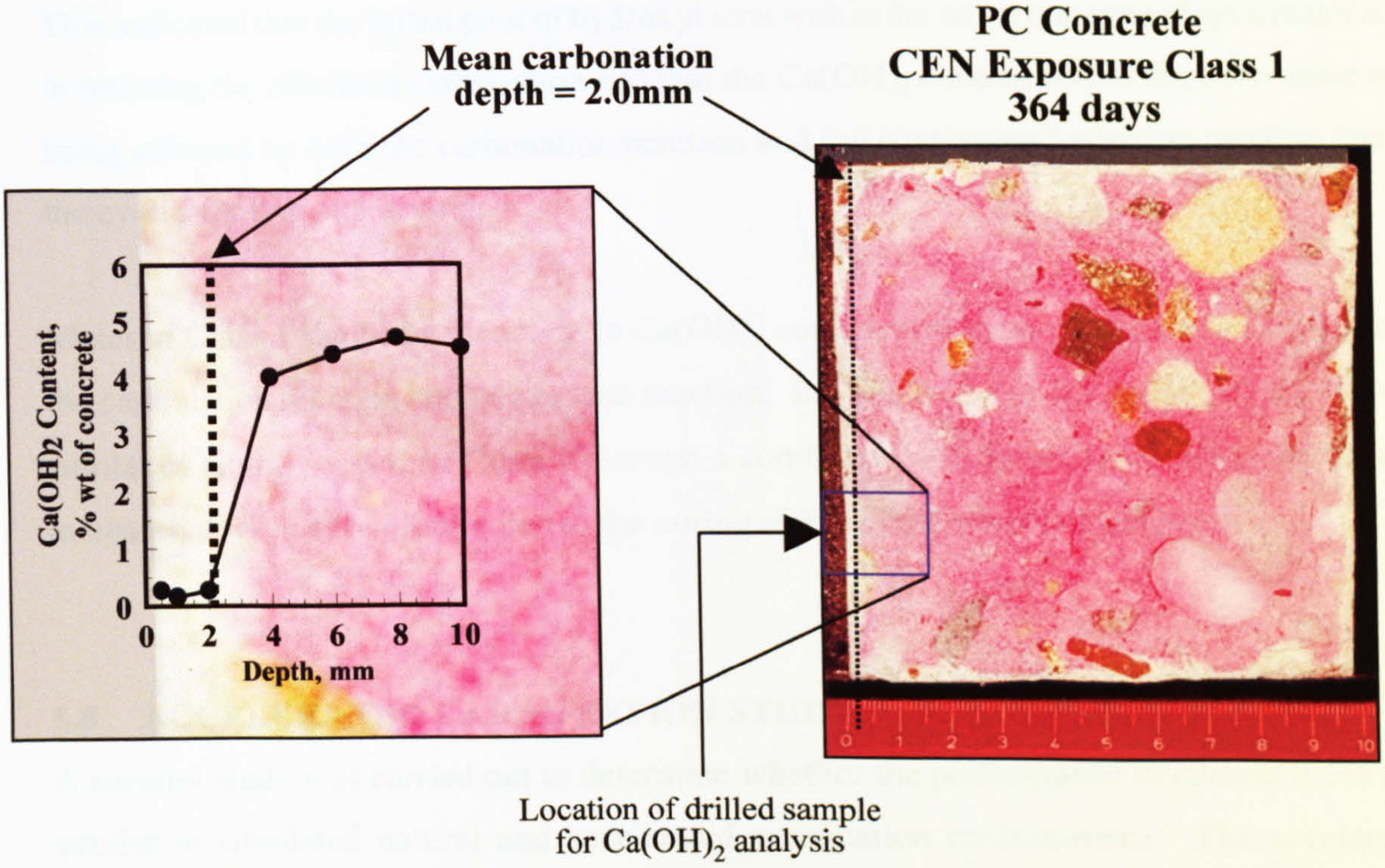


Figure 5.14 Comparison of measured calcium hydroxide profile with depth of carbonation measured by sprayed phenolphthalein on PC concrete. The depth of carbonation corresponds to a sharp increase in the total calcium hydroxide within the outer 10mm of the concrete.

Table 5.14 Total calcium hydroxide at pre-entry and after 2 years exposure in CEN environment in Exposure Classes 1, 2 and 3.

Mix [1]	**Total $Ca(OH)_2$, % wt of cover zone concrete**			
	Pre-entry	After 2 year CEN Storage		
		Class 1	Class 2	Class 3
PC	5.2	4.3	5.0	5.6
MK 10%	4.3	1.2	1.9	2.5
PC/PFA 30%	1.7	0.7	1.2	1.6
CSF 10%	1.5	0.5	1.4	1.7
MK 15%	1.6	0.6	0.9	1.1
CSF 15%	1.4	0.5	0.5	1.2
CSF 20%	1.3	0.5	0.5	1.1
MK 20%	1.3	0.6	0.5	1.0

[1] Mixes are ranked in same order as per depth of carbonation at 2 years (ie PC lowest to MK 20% highest).

This indicated that the initial pool of hydroxyl ions within the cover concrete plays a major role in resisting the effects of carbonation and that the $Ca(OH)_2$ content within the cover zone was being affected by both the carbonation reaction and the continuing hydration reaction due to the cyclic wetting and drying.

Mixes in Class 1 showed a reduction in $Ca(OH)_2$ content with time through a combination of the carbonation reaction and pozzolanic reaction. In Classes 2 and 3, $Ca(OH)_2$ contents were similar or slightly less than Class 1 through a combination of lower carbonation depths and increased degree of hydration due to the curing effect of the moisture present.

5.8 ACCELERATED CARBONATION STUDY

A parallel study was carried out to determine whether the performance of cement types was similar in simulated natural and accelerated carbonation environments. The accelerated carbonation tanks had been previously developed at Dundee University (Dhir et al, 1986) and consisted of an increased partial pressure of 4% CO_2, a temperature of 20°C ± 2°C, and a relative humidity of 55%. In order to ensure that concrete was subjected to higher levels of carbon dioxide at a similar maturity, the specimens were seal cured at a temperature of 20°C ± 2°C for a period of 28 days. All mixes were normalised using the procedure developed for the CEN carbonation test and compared on an equal 28 day compressive strength of 37N/mm^2.

Figure 5.15 shows the depth of carbonation after 20 weeks in the accelerated carbonation test chamber. As with the simulated natural carbonation test, the PC concrete shows the lowest depth of carbonation, however, the relative ranking compared to the Reference Mix is slightly different. The MK10% concrete showed a similar performance to the CSF10% mix suggesting that the carbonation reaction in higher levels of CO_2 may be different to that in levels typical to the natural environment (Buenfeld et al, 1996). The higher partial pressures of CO_2 have been found to lead to the formation of bicarbonates which in turn produce further carbonation as the ingress of CO_2 proceeds (Richardson, 1988).

A comparison between CEN Exposure Class 1 carbonation and accelerated carbonation was carried out to ascertain whether 1 year and 2 year CEN carbonation depths could be estimated from the 20 week accelerated carbonation. Figure 5.16 shows that the correlation between CEN exposure and accelerated exposure is reasonable, having a Pearson correlation coefficient of 0.79 at 1 year and 0.87 at 2 years.

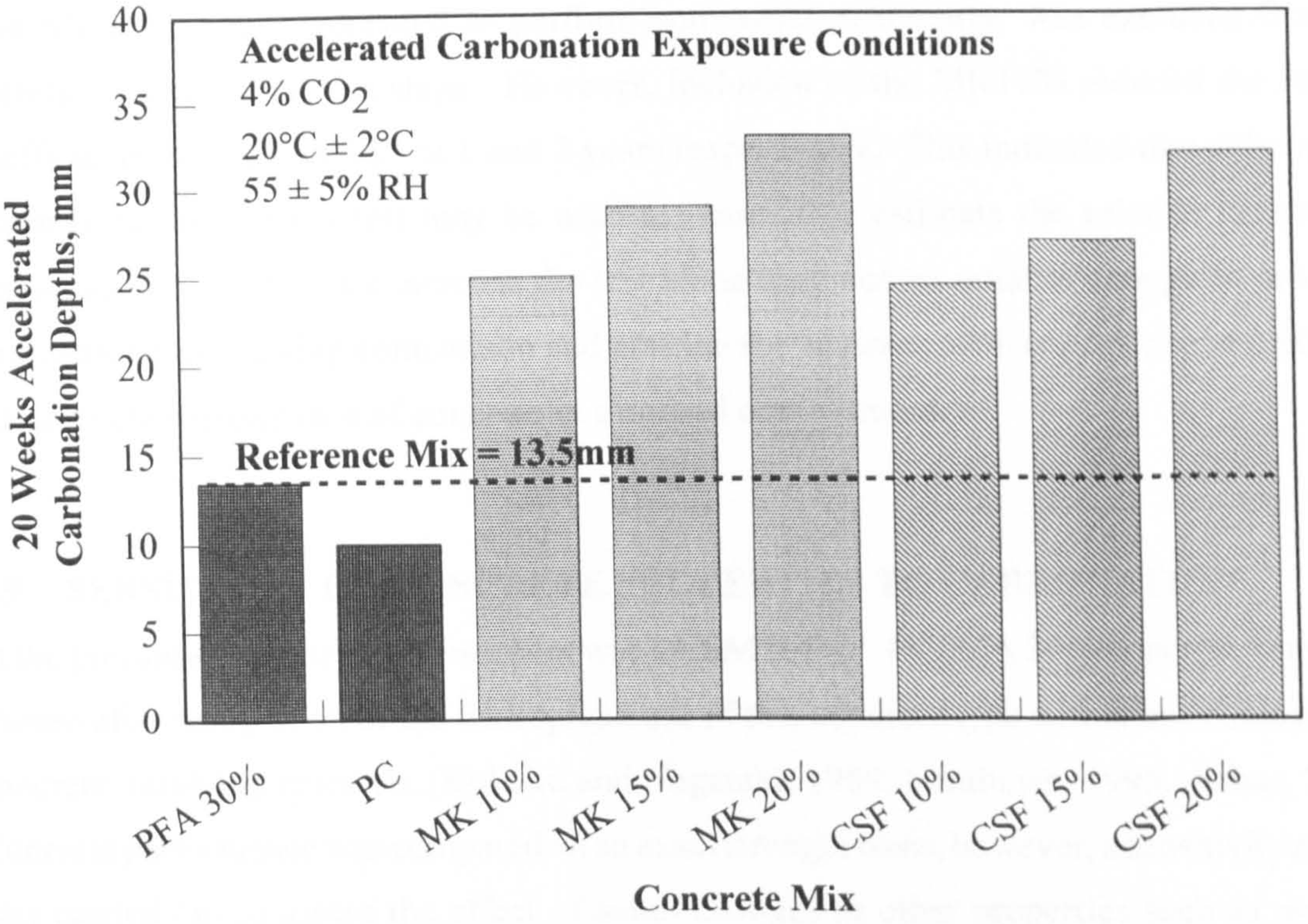


Figure 5.15 Accelerated carbonation depths of Series 1 Test Mixes after 20 weeks exposure. All specimens were seal cured for 28 days prior to exposure.

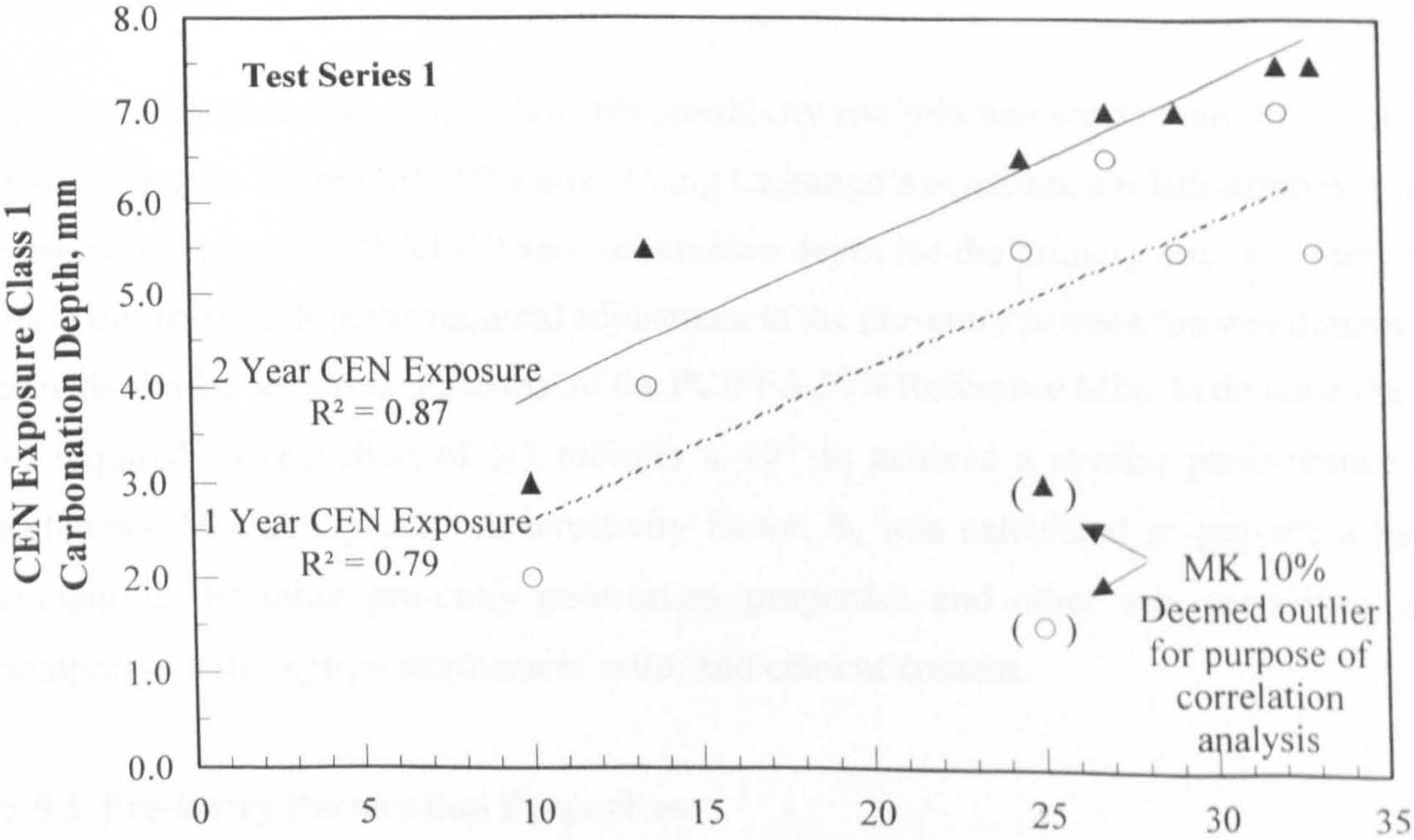


Figure 5.16 Correlation between CEN Exposure Class 1 carbonation depths at 1 year and 2 years and 20 weeks accelerated carbonation depths. MK 10% is not included in correlation analysis.

The MK10%, which appeared to perform somewhat differently, was excluded from the correlation analysis at this stage. However, inclusion of the MK10% reduced the Pearson coefficients to 0.48 and 0.51 at 1 and 2 years respectively. This indicated that although the accelerated carbonation test may be used to reasonably estimate the relative carbonation performance of different concretes, the test alone may not be reliable enough to provide a confident benchmarking comparison and provide the engineer with confidence in predicting the absolute performance of concrete in a natural environment.

5.9 SENSITIVITY OF CONCRETE PROPERTIES TO CARBONATION

In the present study, the Reference Mix was a CEM II/B-V PC/PFA 30% concrete which was chosen after recognition of the widespread use of this concrete type within both industry and concrete durability research. (Kokubu and Nagataki, 1989, Matthews, 1995, Abbas, 2000). Concrete performance was compared on an exact strength basis, however, a sensitivity analysis was carried out to assess the effect of small changes in other properties such as pre-entry permeation and compressive strength in relation to carbonation performance in order to ascertain the dependency of particular concrete properties on performance. The analysis also examined the required adjustments in such properties to achieve similar performance to the Reference Mix.

Figure 5.17gives an example of how the sensitivity analysis was carried out for the pre-entry ISAT-10 results for the MK 15% mix. Using Lagrange's equation, a relationship was formed between the pre-entry ISAT-10 and carbonation depth for the primary and secondary mixes. From this relationship, the required adjustment to the pre-entry permeation was determined to provide similar performance to that of the PC/PFA 30% Reference Mix. In this case the ISAT-10 required an reduction of 5.5 $ml/m^2/s \times 10^{-3}$ to achieve a similar performance to the Reference Mix at 2 years. A sensitivity factor, S, was calculated to provide a basis for comparing the other pre-entry permeation properties and other mix properties such as compressive strength, water/cement ratio, and cement content.

5.9.1 Pre-Entry Permeation Properties

Figure 5.18 compares the sensitivity analysis of the pre-entry permeation properties of CEM II concretes. For the majority of CEM II concretes, namely MK 15%, MK 20%, and CSF mixes, a reduction in permeation properties was required to achieve similar performance. The 'S' factors were very similar in magnitude for intrinsic air permeability and water vapour diffusivity.

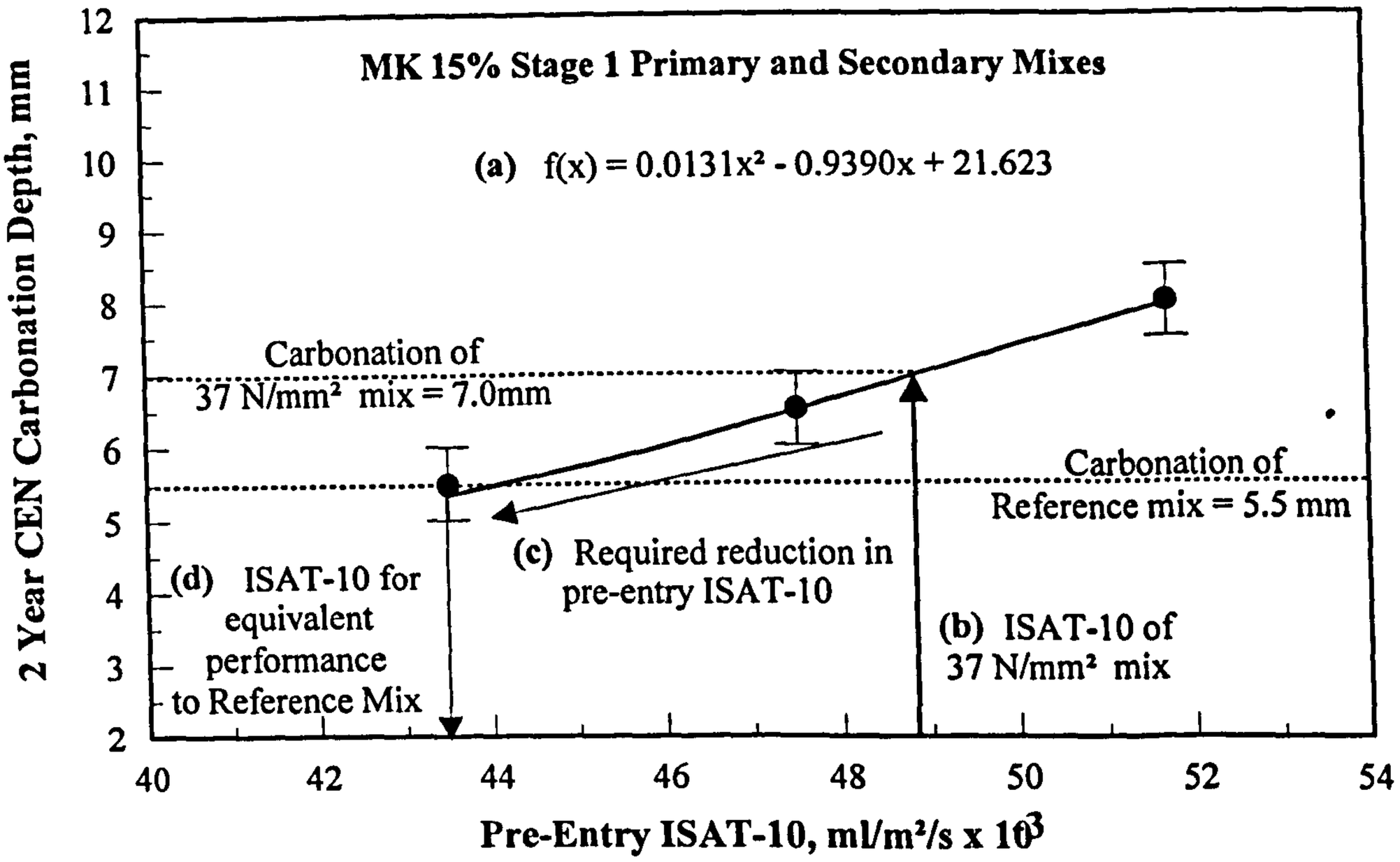


Figure 5.17 Example of sensitivity analysis of MK 15% concrete with respect to pre-entry ISAT-10.

(a) The curvilinear relationship between ISAT-10 and carbonation depth is determined by Lagrange's Formula:

$$f(x) = \frac{(x-x_1)(x-x_2)}{(x_0-x_1)(x_0-x_2)} f_0 + \frac{(x-x_0)(x-x_2)}{(x_1-x_0)(x_1-x_2)} f_1 + \frac{(x-x_0)(x-x_1)}{(x_2-x_0)(x_2-x_1)} f_2$$

Where: (x_1, f_1), (x_0, f_0), (x_2, f_2) are (47.5, 6.5) and (51.5, 7.5) &(43.5, 5.5) for the primary and secondary mixes respectively in this example.

(b) The ISAT-10 for the normalised 37N/mm^2 mix is determined.

(c) From the relationship between the ISAT-10 and carbonation depth, the increase in ISAT-10 required to achieve similar performance to the Reference Mix is found.

(d) The pre-entry ISAT-10 is read from the x-axis.

(e) The sensitivity factor is determined $S_{ISAT} = \frac{Adjusted\ ISAT\text{-}10}{Original\ ISAT\text{-}10} = 0.9$

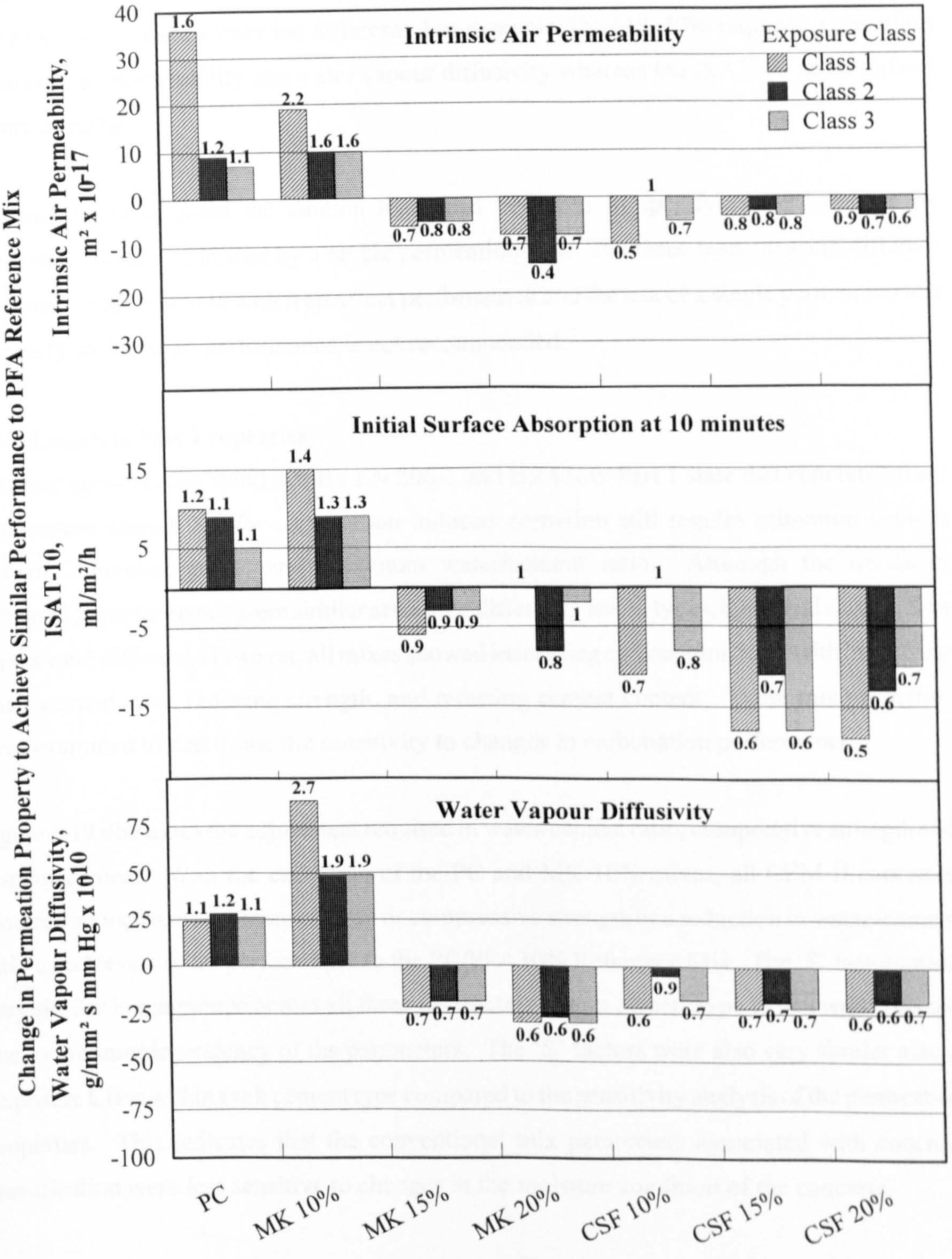


Figure 5.18 Sensitivity analysis of pre-entry permeation properties to achieve similar carbonation performance as PFA Reference mix. *Note: data labels are Sensitivity factors to achieve similar performance as PFA Reference mix.*

Although the trends for ISAT-10 were similar to that of other permeation tests, the magnitudes of the 'S' factors were somewhat different. For example, the MK 20% required a reduction in intrinsic air permeability and water vapour diffusivity whereas the ISAT-10 value did not require a change.

The analysis highlighted the caution that must be taken in specifying performance by permeation alone and indeed by a single permeation test. The three tests measure different properties of the concrete which all affect performance and the use of a single permeation test to specify carbonation performance is not recommended.

5.9.2 Concrete Mix Properties

Concrete specification standards BS EN 206-1 and BS 8500: Part 1 state that concrete mixes in exposure classes XC for carbonation induced corrosion still require minimum cement content, minimum grade, and maximum water/cement ratio. Although the trends in carbonation performance were similar across the different cement types, the actual carbonation depths were different. However, all mixes showed increasing carbonation depth with increasing water/cement ratio, reducing strength, and reducing cement content. These mix properties were examined to determine the sensitivity to changes in carbonation performance.

Figure 5.19 illustrates the adjustment required in water/cement ratio, compressive strength and cement content. With the exception of the PC and MK 10% mixes, all CEM II concretes required an increase in cement content or compressive strength or a reduction in water /cement ratio to achieve similar performance to the PC/PFA30% Reference Mix. The 'S' factors were very similar in magnitude across all three parameters within cement type which was expected due to the interdependency of the parameters. The 'S' factors were also very similar across Exposure Class within each cement type compared to the sensitivity analysis of the permeation properties. This indicates that the conventional mix parameters associated with concrete specification were less sensitive to changes in the moisture condition of the concrete.

Concrete mix parameters such as water/cement ratio, cement content, and compressive strength are properties which have been used to specify concrete durability for a number of years within standards (Concrete Society, 1999). However, these parameters may not be sufficient in specifying concrete in a carbonating environment. The variety of cement types now available and potential different hydration characteristics will give rise to different concrete properties for a single mix parameter, for example, water/cement ratio.

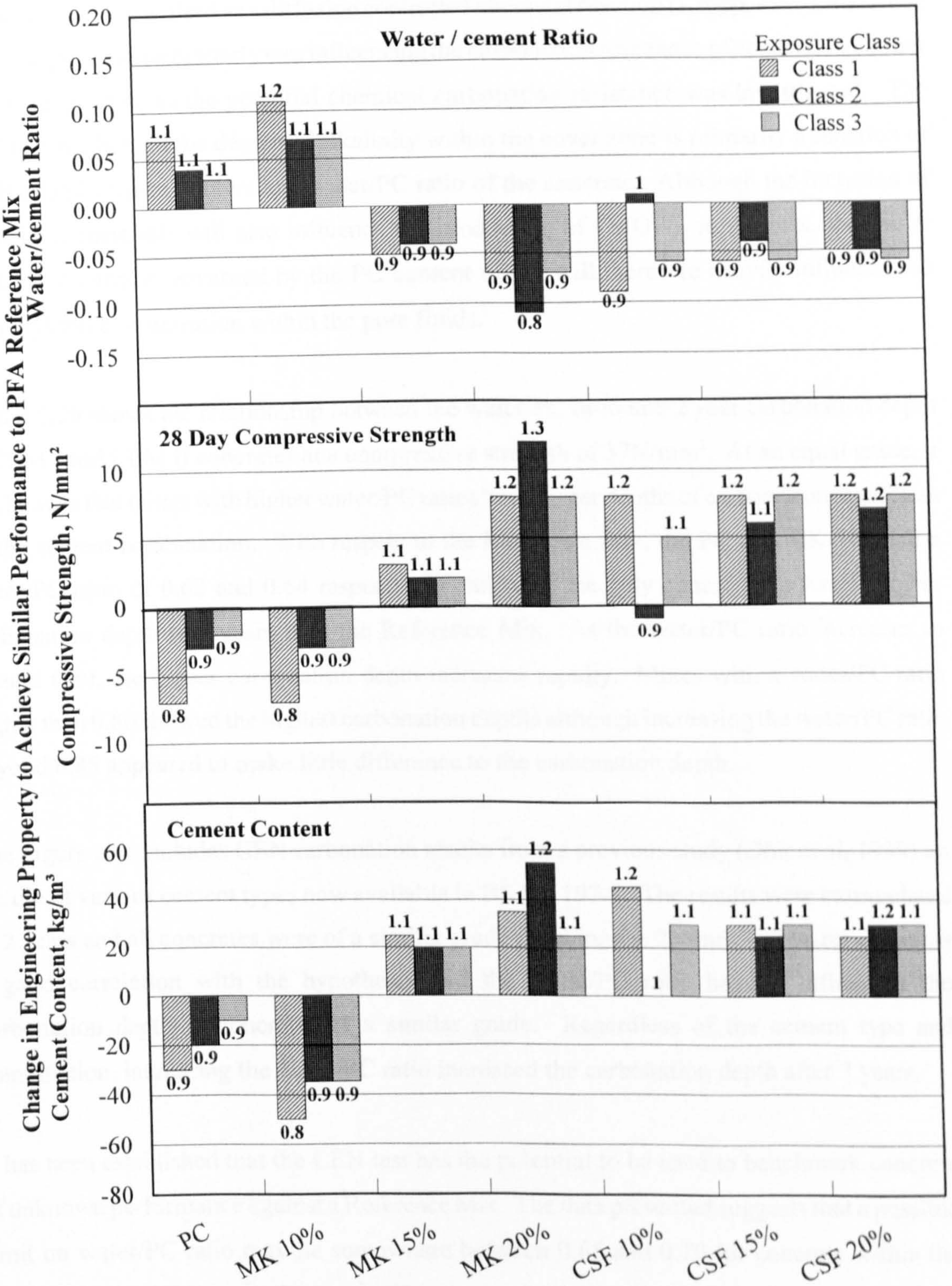


Figure 5.19 Changes required in water/cement ratio, compressive strength and cement content to achieve similar carbonation performance to the PC/PFA30% Reference Mix.
Note: data labels are Sensitivity factors to achieve similar performance as PFA Reference mix.

Carbonation is recognised as a diffusion controlled chemical reaction (Kropp, 1995), and since no single permeation property was influencing the carbonation resistance of concrete, a further parameter relating to the potential chemical carbonation resistance was investigated. The driving force behind the degree of alkalinity within the cover zone is primarily a function of the Portland cement content and water/PC ratio of the concrete. Although the inclusion of pozzolanic materials will also influence the production of $Ca(OH)_2$ in the mix, the initial $Ca(OH)_2$ content is governed by the PC content which will therefore heavily influence the hydroxyl ion concentration within the pore fluids.

Figure 5.20 shows the relationship between the water/PC ratio and 2 year carbonation depth of CEM I and CEM II concretes at a compressive strength of 37N/mm^2. At an equal grade, it can be seen that mixes with higher water/PC ratios have larger depths of carbonation regardless of the cement combination. With respect to the Reference Mix, the PC and MK10% had a water/PC ratio of 0.62 and 0.64 respectively and were the only concretes to have a lower carbonation depth at 2 years than the Reference Mix. As the water/PC ratio increases to around 0.80, the 2 year carbonation depth increases rapidly. Mixes with a water/PC ratio higher than 0.80 showed the highest carbonation depths although increasing the water/PC ratio beyond 0.85 appeared to make little difference to the carbonation depth.

The Figure also includes CEN carbonation results from a previous study (Dhir et al, 1999) on the use of various cement types now available in BS EN 197-1. The results were extrapolated to 2 years and all concretes were of a similar grade (37N/mm^2 ± 2N/mm^2). The results show a good correlation with the hypothesis that the water/PC ratio heavily influences the carbonation depth in concretes of a similar grade. Regardless of the cement type and combination, increasing the water/PC ratio increased the carbonation depth after 2 years.

It has been established that the CEN test has the potential to be used to benchmark concrete of unknown performance against a Reference Mix. The data presented suggests that a possible limit on water/PC ratio may lie somewhere between 0.65 and 0.70 for concrete within the range of grades 37N/mm^2 ± 2N/mm^2 . This range of concrete grades incorporates the limiting grades stated in BS EN 206-1 (37N/mm^2) and BS 8500 (35N/mm^2). Here, a tentative limiting water/PC ratio of 0.65 has been suggested in Exposure Class 1.

Figure 5.21 shows the relationship between water/PC ratio and 2 year CEN carbonation depths in Exposure Classes 2 and 3.

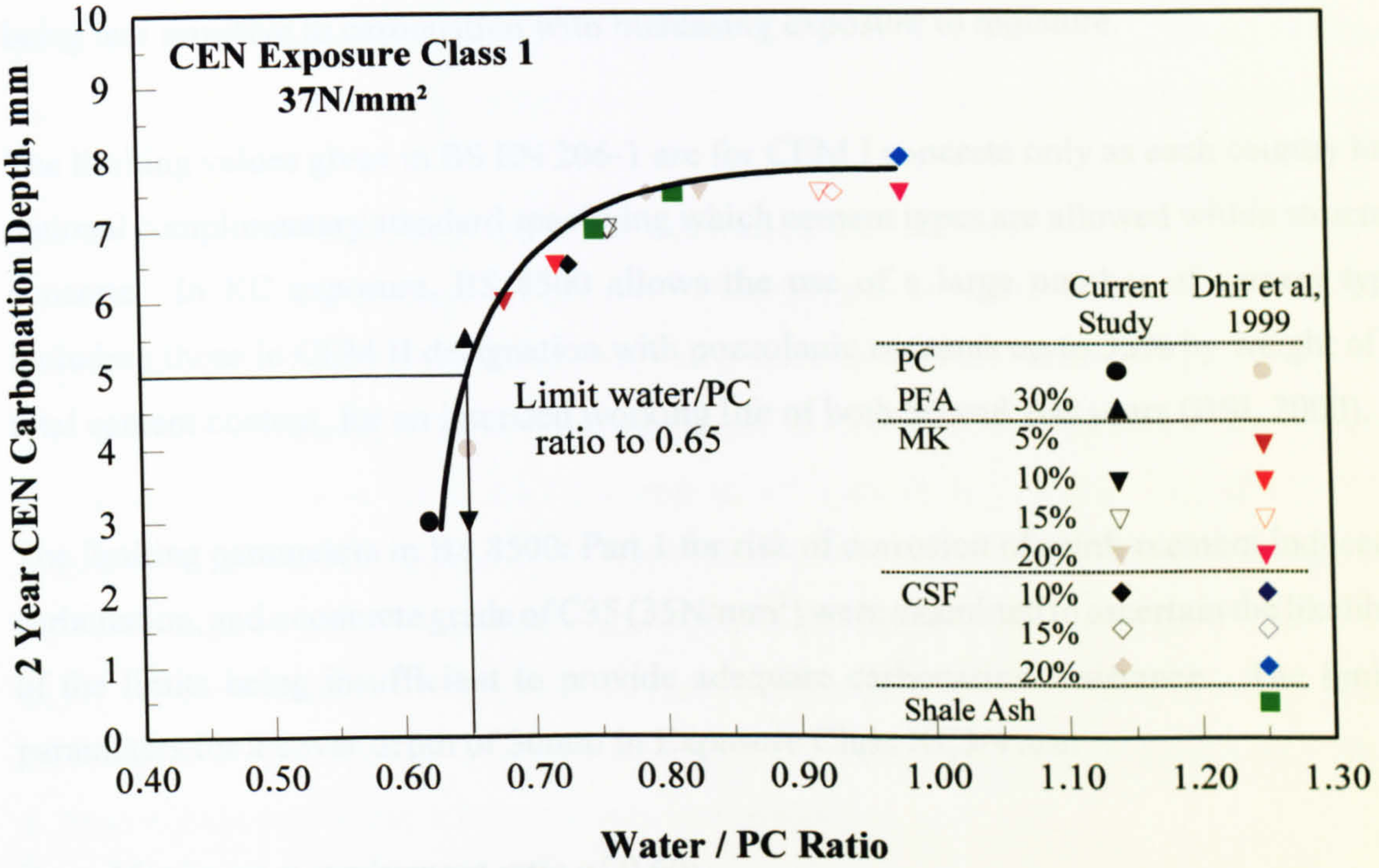


Figure 5.20 Relationship between water/PC ratio and 2 year CEN carbonation depth for CEM I and CEM II concrete in Exposure Class 1.

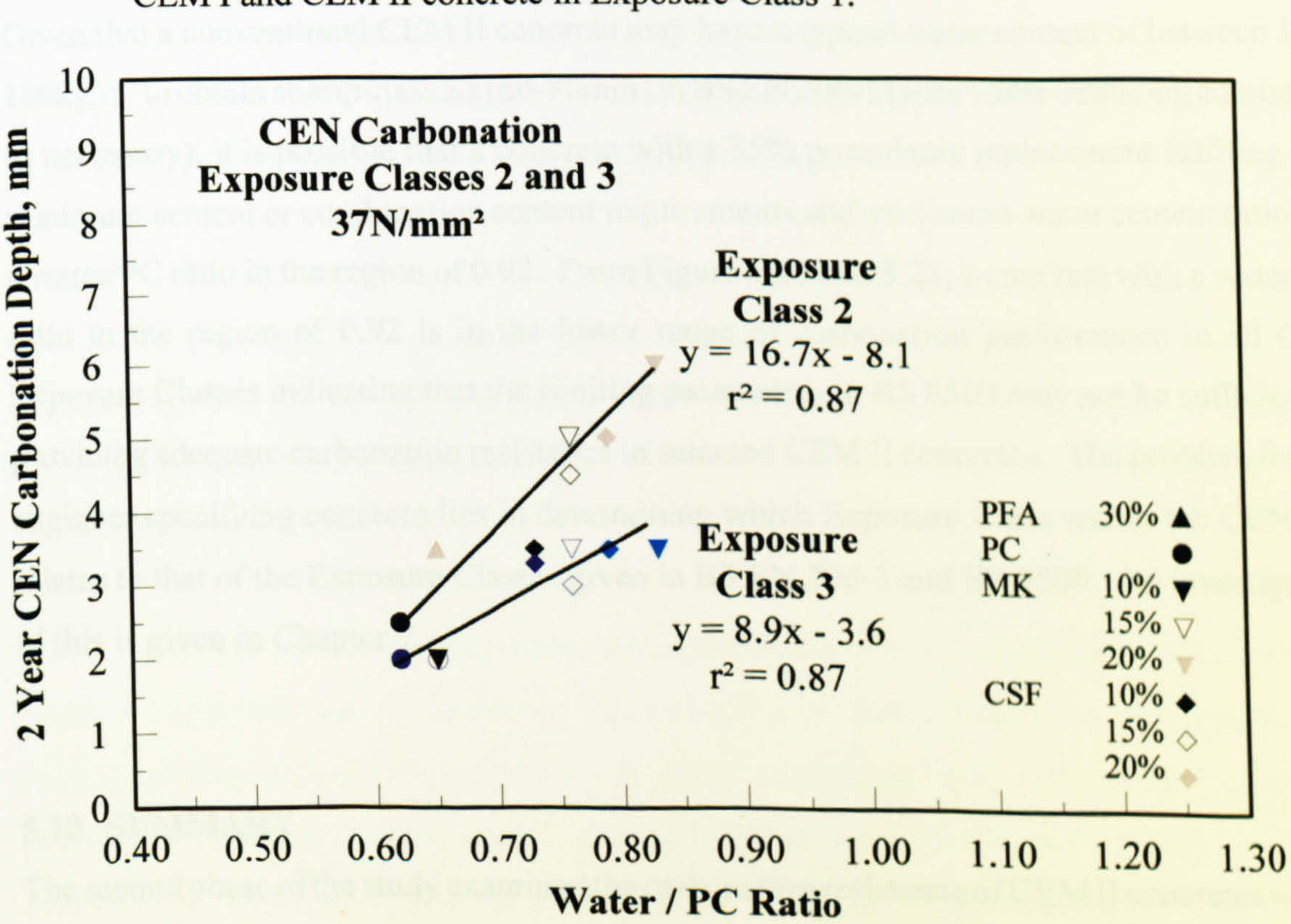


Figure 5.21 Relationship between water/PC ratio and 2 year CEN carbonation depth for CEM I and CEM II concrete in Exposure Classes 2 and 3.

The relationship is linear compared to that in Exposure Class 1 with changes in water/PC ratio being less sensitive to carbonation with increasing exposure to moisture.

The limiting values given in BS EN 206-1 are for CEM I concrete only as each country has a national complimentary standard specifying which cement types are allowed within structural concrete. In XC exposure, BS 8500 allows the use of a large number of cement types, including those in CEM II designation with pozzolanic contents up to 35% by weight of the total cement content, for an intended working life of both 50 and 100 years (BSI, 2000).

The limiting parameters in BS 8500: Part 1 for risk of corrosion of reinforcement induced by carbonation, and a concrete grade of C35 (35N/mm^2) were examined to ascertain the likelihood of the limits being insufficient to provide adequate carbonation resistance. The limiting parameters for a cover depth of 30mm in Exposure Class XC3/4 are:

i) Maximum water/cement ratio of 0.60;
ii) Minimum cement or combination content of 280kg/m^3.

Given that a conventional CEM II concrete may have a typical water content of between 170-180kg/m^3 to obtain slump class S2 (60-90mm) in BS EN 206-1 (with water-reducing admixture as necessary), it is possible that a concrete with a 35% pozzolanic replacement fulfiling the minimum cement or combination content requirements and maximum water cement ratio has a water/PC ratio in the region of 0.92. From Figure 5.20 and 5.21, a concrete with a water/PC ratio in the region of 0.92 is in the lower range of carbonation performance in all CEN Exposure Classes indicating that the limiting parameters in BS 8500 may not be sufficient in providing adequate carbonation resistance in selected CEM II concretes. The problem for the engineer specifying concrete lies in determining which Exposure Class within the CEN test relates to that of the Exposure Classes given in BS EN 206-1 and BS 8500. An investigation of this is given in Chapter 7.

5.10 SUMMARY

The second phase of the study examined the carbonation resistance of CEM II concretes which, although not presently readily used within the UK, may potentially be in the future. The concretes containing MK and CSF were compared on an equal strength basis using a previously developed normalisation procedure.

All concretes were seal cured until $0.5f_{cm,28}$ before being placed in the CEN carbonation test chamber. Little difference was observed between the times to reach $0.5f_{cm,28}$ in seal curing and standard moist curing with the exception of MK 10% mix which was sensitive to moist curing.

The effect of cement type on carbonation performance was clearly seen in CEN Exposure Class 1. The 2 year carbonation depths of CEM II concretes containing MK and CSF were larger than the PC/PFA30% Reference Mix, with carbonation depths increasing with increasing MK and CSF replacement level. The exception to this was the MK 10% which showed a similar performance to the CEM I concrete at all ages up to 2 years. The effect of CEN Exposure Class was also apparent with carbonation depths reducing in all cases with increasing exposure to moisture. In Exposure Class 3 (concrete stored under water for 6 hours every 7 days), the performances of CEM I and CEM II concretes were very similar, with a range of carbonation depths between 2.0mm and 3.5mm at 2 years compared to a range of 3.0mm to 7.5mm in Exposure Class 1 (no exposure to moisture).

A statistical analysis of the carbonation data showed that the change in relative ranking of cement types in Exposure Class 1 (up to 18 months) and Exposure Class 2 (up to 12 months) was statistically significant. After these points, there was no change in ranking, indicating a degree of statistical stability within the test method. The carbonation depths were also found to be normally distributed both within each prism and across each prism set.

Permeation testing over the test period indicated that the permeation properties, ISAT-10, intrinsic air permeability, and water vapour diffusivity, were reducing with time. Pre-entry permeation alone did not give a good correlation with carbonation performance of CEM I or CEM II concrete, raising doubts whether a single permeation test is sufficient as use as an initial type approval test.

A reasonable correlation was found between 6 hour absorption at 7 days and 2 year carbonation depth in Exposure Class 1. However, the coefficient of determination reduced significantly with increasing exposure to moisture. A better correlation was found between depth of moisture penetration at 7 days and 2 year carbonation depth, indicating that the absorptive properties of the concrete may not give a true reflection of the near surface pore structure.

The outer 10mm of the concrete showed an increase in the degree of hydration with increasing exposure to moisture. This was expected as reactivation of unhydrated cement particles is not

uncommon in dry concrete which is subjected to wetting (Neville, 1996). As the permeation properties alone did not indicate carbonation performance, the total $Ca(OH)_2$ within the cover zone showed a reasonable correlation with the ranking of carbonation performance within Exposure Class 1. Sharp increases in $Ca(OH)_2$ in the cover zone corresponded to the measured carbonation depths in the concrete, indicating that the neutralisation effect is primarily a function of the reaction between the CO_2 and $Ca(OH)_2$.

A parallel accelerated carbonation study of the CEM II concrete showed that although the relative ranking of cement types was slightly different to the CEN carbonation test, a coefficient of determination of 0.87 was found between 20 weeks accelerated carbonation and 2 year CEN carbonation. The exception was again the MK 10% mix.

The mix parameters commonly used limit durability in specification standards, water/cement ratio, compressive strength, and cement content, were examined. No common parameter was found to determine the carbonation performance, and a further parameter which reflected the cover zone pore fluid alkalinity was examined. The water/PC ratio demonstrated potential use as a factor to specify carbonation performance, since it may define the amount of $Ca(OH)_2$ that can be provided by calcium silicate hydration.

CHAPTER 6

INFLUENCE OF AGGREGATE TYPE AND FINES CONTENT ON CARBONATION RESISTANCE

6.1 INTRODUCTION

The testing undertaken in the pan-European Round Robin by CEN showed a degree of variability in results which was attributed to a number of factors including variations in material characteristics. The third phase of the current study examined the effect of varying the coarse aggregate type on carbonation resistance of the PC/PFA30% Reference Mix. The effects of three different coarse aggregate types, commonly used within the UK and conforming to BS 882 1992, were examined, along with the effect of adjusting the water content of the mix or using a normal range plasticizing admixture to attain the required workability. As CEM II concretes in BS EN 197-1 contain a proportion of fine material, through the use of fillers or additions to the cement such as CSF or PFA, the role of the fine particulate material within the concrete was also examined. The effect of adjusting the fine/coarse aggregate ratio was studied to determine the role that the ratio plays in defining the physical and chemical characteristics of the concrete. The packing densities of the CEM II concretes were also examined using an integrated particle packing and hydration model, and the effect of increasing the fines content of the concrete by replacing the fine aggregate with limestone filler was examined, to determine the benefits that might be obtained by consideration of the physical characteristics of the constituent material.

6.2 EFFECT OF COARSE AGGREGATE TYPE

Three additional coarse aggregate types commonly used within the UK were tested to ascertain their effect on the carbonation resistance of hardened concrete. PC/PFA 30% mixes were designed using Thames Valley gravel, crushed granite and crushed limestone for comparison on an equal strength basis. Mixes proportioned using crushed rock were designed with both an increased water content (to obtain the desired workability) and an unadjusted water content in combination with a normal range plasticizing admixture, and compared to the Reference Mix to determine whether the use of a plasticizing admixture affected the carbonation resistance.

6.2.1 Test Series 2: Normalised Mix Proportions

Table 6.1 gives the constituent proportions for the concrete mixes in Test Series 2. The proportions are normalised to 37N/mm^2 using the procedure detailed in Chapter 4.

The alternative gravel source required a slight increase in cement content, compared with the bulk gravel source, to achieve a 28 day compressive strength of 37N/mm^2. This was attributed to fact that the majority of the particles in the Thames Valley gravel had a very smooth surface texture. On testing for compressive strength, it was noted that failure was primarily at the interfacial bond between the smooth surface textured coarse aggregate and cement paste. Mixes containing crushed rock had lower cement contents than the gravel mixes in both the water adjusted and plasticized mixes due to the angular nature and coarse surface texture of crushed aggregates, which contribute to the compressive strength of concrete by improving the interfacial bond (Basheer, 1991).

The compressive strength developments of Test Series 2 Mixes were similar, with all mixes having a medium strength development in accordance with BS BS EN 206-1, with 2/28 day ratios ranging from 0.30 to 0.32.

6.2.2 Effect of Coarse Aggregate Type on CEN Carbonation

Across all coarse aggregate types, the rate of carbonation up to 2 years appeared to be very similar in comparison to the Reference Mix containing the local source of gravel. Figure 6.1 shows the 2 year carbonation depth of all mixes in Test Series 2. The alternative gravel source, Mix AG2, had a slightly higher depth of carbonation compared to the Reference Mix in all three Exposure Classes.

The two crushed aggregate sources with a varied water content gave slightly better performance than the gravel mixes in Exposure Class 1. However, with increasing exposure to moisture, the performance was very similar, and this was reflected in the accelerated carbonation testing, Figure 6.1.

From the results of the CEN carbonation test, it appeared that the effect of coarse aggregate type was negligible on carbonation performance. However, closer inspection of the mix properties suggested that coarse aggregate type had an influence on carbonation performance.

Table 6.1 Normalised mix constituent proportions for Test Series 2 Mixes.

Cement Type	Normalised Mix Constituent Proportions, kg/m³					Plasticizer Dosage, l/100kg Cement	w/c ratio
	Total Cement Content	Water [1]	Aggregates: Sand [2]	Aggregates: 10 mm	Aggregates: 20 mm		
Reference Mix [3] - *AG1*							
PC/PFA 30%	375	170	640	400	800	-	0.46
Non Plasticized Mixes							
Thames Valley Gravel - AG2							
PC/PFA 30%	385	170	630	400	800	-	0.44
Crushed Granite - AG3							
PC/PFA 30%	345	190	650	400	800	-	0.55
Crushed Limestone - AG4							
PC/PFA 30%	340	190	655	400	800	-	0.56
Plasticized Mixes							
Crushed Granite - AG3P							
PC/PFA 30%	310	170	700	400	800	0.30	0.55
Crushed Limestone - AG4P							
PC/PFA 30%	305	170	705	400	800	0.33	0.56

(1) Free water content to achieve slump class S2 to BS EN206-1 (60-90mm). Plasticizer used as shown.

(2) Natural sand, zone M grading to BS 812:1992.

(3) Coarse aggregate is natural gravel.

Mixes AG3P and AG4P had significantly lower cement contents than the Reference Mix, yet the performance was similar in all Exposure Classes.

A similar phenomenon was observed in mixes AG3 and AG4, although to a lesser extent. Table 6.2 provides the pre-entry permeation and total $Ca(OH)_2$ content within the outer 10mm cover zone.

The pre-entry permeation properties reflected the differences in carbonation resistance measured by phenolphthalein. The alternative gravel source, mix AG2, showed the greatest permeation properties when compared to the other aggregate sources, and also presented a slightly poorer resistance to carbonation compared to the other coarse aggregate sources. Mix AG2 required a slightly higher cement content than the Reference Mix and the resulting higher carbonation depths were attributed to the increased pre-entry permeation properties.

The chemical and physical effects of using different coarse aggregate sources were apparent in Test Series 2 mixes, although the spread of carbonation depths was only 1.0mm after 2 years in Exposure Class 1. Although mixes containing crushed rock had a lower cement content and higher water/PC ratio than the Reference Mix, the potential for poor carbonation resistance through a reduced calcium hydroxide concentration within the cover zone was offset by the improved physical properties of the cover zone. This once again highlighted the importance of both the physical and chemical characteristics of concrete in providing carbonation resistance, and the Series demonstrated that the coarse aggregate type might indirectly influence the carbonation resistance of concrete through changes in the mix design.

6.3 INFLUENCE OF FINE AGGREGATE CONTENT

6.3.1 Introduction

The mixes in Test Series 1 showed that cement type can influence the carbonation resistance of hardened concrete. Mixes containing higher replacement levels of MK and CSF exhibited poorer performance than PC mixes, and this was attributed to a combination of the physical and chemical characteristics of the concrete cover zone. An investigation of calcium hydroxide content and permeation properties, in terms of absorption, diffusion, and permeability, showed that, although the concrete mixes with poorer carbonation performance had relatively good permeation properties, the lower initial levels of alkaline constituents in the cover zone led to increased carbonation performance.

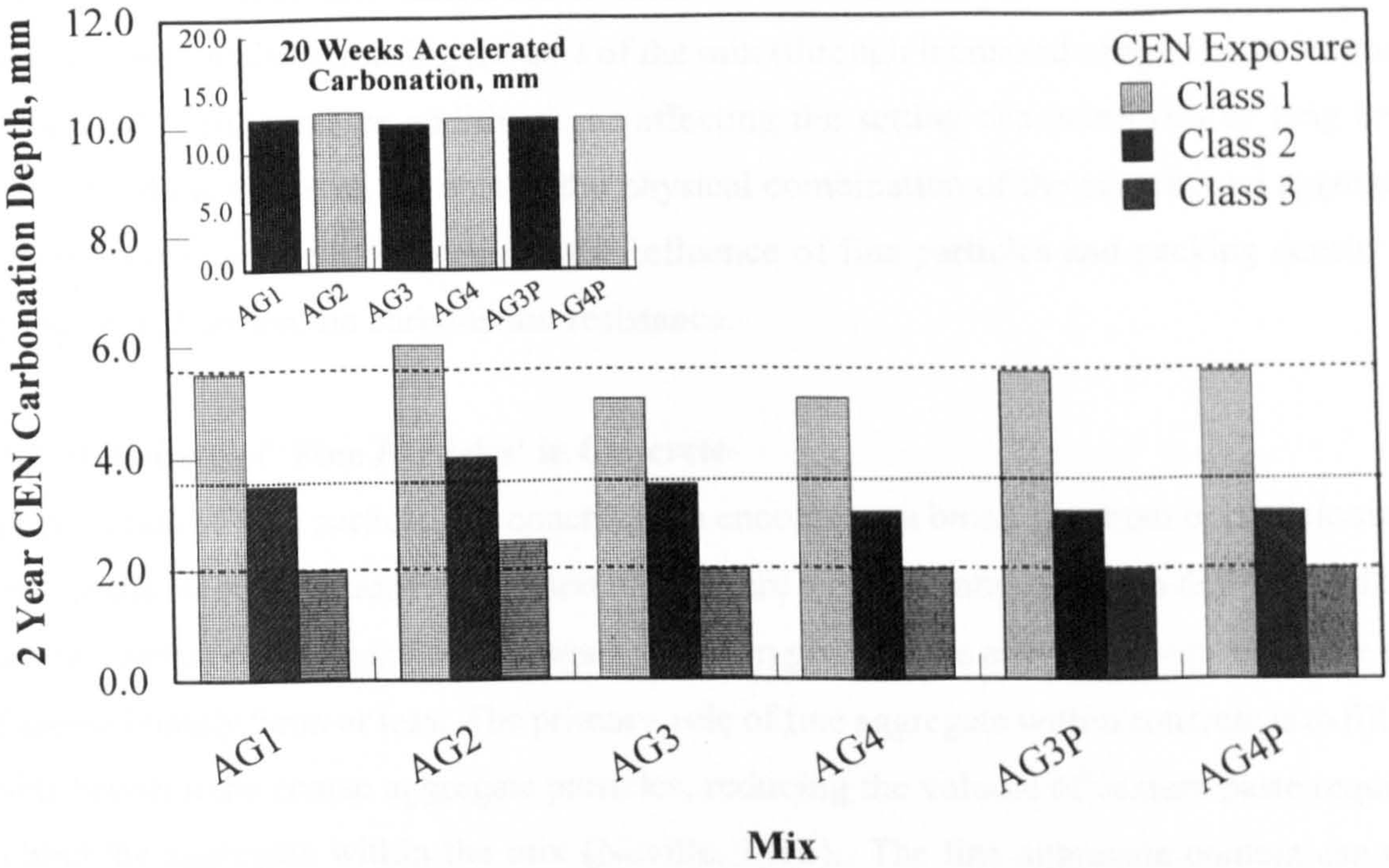


Figure 6.1 Comparison of 2 year CEN and 20 weeks accelerated carbonation depths normalised to 37N/mm^2 for Test Series 2 mixes.

Table 6.2 Physical and chemical characteristics of Test Series 2 mixes prior to placement in the CEN Test chamber.

Mix	**Pre-Entry Permeation Properties**			
	WVD x 10^{-10} g/mm s Hg	**ISAT-10,** ml/m^2/s x 10^{-2}	**Intrinsic Air Permeability,** m^2 x 10^{-17}	**Pre-Entry Total Ca(OH)$_2$,** % wt of cover zone concrete[1]
AG1	112.0	55.4	35.0	1.7
AG2	130.5	60.0	47.5	2.0
AG3	100.5	50.3	30.4	1.4
AG4	102.5	50.0	32.3	1.4
AG3P	98.9	48.1	30.0	1.2
AG4P	97.6	47.3	30.5	1.2

(1) Measured to a depth of 10mm

As it is often difficult and dangerous to increase the alkalinity of the concrete cover zone without significantly increasing the cost of the mix (through increased cement content or use of chemical admixtures or additives), or affecting the setting characteristics or long term durability of the concrete, the role of the physical combination of the cement and aggregate particles was examined to determine the influence of fine particles and packing density of aggregate and cement on carbonation resistance.

6.3.2 Definition of 'Fine Particles' in Concrete

The definition of 'fine particles' in concrete can encompass a broad spectrum of particle sizes. Some of the main definitions are illustrated in Figure 6.2. The most common definition of fine particles within concrete is fine aggregate, the term given to the aggregate with a particle size of approximately 5mm or less. The primary role of fine aggregate within concrete is to fill the voids between the coarse aggregate particles, reducing the volume of cement paste required to bind the aggregate within the mix (Neville, 1996). The fine aggregate content can also govern the workability of fresh concrete and the propensity for segregation of the coarse aggregate and fresh cement paste to occur (Neville, 1996).

Many researchers have investigated the effects of particle packing on concrete mix design and durability (Glavind et al, 1993; Goltermann et al, 1997; Dewar, 1998), although the physical and chemical roles of much finer materials, typically particles less than 125 μm within the fine aggregate and cement, are generally ill defined. Table 6.3 summarises the definitions of fine particles as will be referred to throughout this section of the study.

6.3.3 Test Series 3: Adjusted Fine / Coarse Aggregate Ratio Mixes

The proportion of fine aggregate within concrete depends on a number of factors such as grading of coarse aggregate, fineness and grading of fine aggregate, and required workability (Teychenné et al, 1997). Common mix design procedures determine the fine aggregate content in terms of the fine to coarse aggregate ratio (Teychenné et al, 1997, Hughes, 1971). The mixes in the current study were designed using the Teychenné et al (1997) method, and the ratio of fine / coarse aggregate was dependent on:

(i) Required workability - to Class S2 (BS EN 206-1);

(ii) Free water/cement ratio of mix - Current study Reference mix = 0.46;

(iii) Proportion of fine aggregate passing a 600μm sieve - Current study - 70%.

With regard to the Reference Mix and the PC mix, the proportion of fine aggregate in the total aggregate was 35%, a fine / coarse aggregate ratio of 0.35. To examine the effect of varying the total fines content of the mix, the fine aggregate content was adjusted by ±10%, producing mixes with a fine/coarse aggregate ratio of 0.25 and 0.45. Both the PC/PFA 30% Reference Mix and the PC mix were examined to determine the effect of the fine/coarse aggregate ratio on the hardened concrete carbonation resistance.

The subsequent mix proportions are given in Table 6.4 and observations of the concrete in its fresh state given in Table 6.5. Mixes with an increased fine/coarse aggregate ratio required a dosage of plasticizer in the region of 3% by weight of cement in order to achieve the desired workability of slump class S2 (60-90mm) in BS EN 206-1.

Closer observation of the mixes with a reduced fine/coarse aggregate ratio revealed a harsh, open mix due to the deficiency of fine particles, although the measured slump still conformed to Slump Class S2 of BS EN 206-1. The harsh nature of the mix was less pronounced in the PC/PFA30% Reference Mix, and this was attributed to the increased cement content and overall fine particle content of the Reference Mix.

6.3.4 Carbonation of Test Series 3 Mixes

Test Series 3 mixes were tested in the CEN Test Chamber for a period of 2 years. All mixes were normalised to a 28 day compressive strength of 37 N/mm². Figure 6.3 illustrates the effect of adjusting the fine/coarse aggregate ratio on the carbonation resistance in Exposure Classes 1, 2 and 3. The mixes with a reduced fine/coarse aggregate ratio exhibited an increased carbonation depth in all three Exposure Classes when compared with the control mixes. This was expected since the mix was very harsh in its fresh state, and a certain degree of segregation and bleeding had occurred when the specimens were cast. In reality, a fine/coarse aggregate ratio of 0.25 would represent the very lowest fine/coarse aggregate ratio boundary for a conventional concrete.

The mixes with increased fine/coarse aggregate ratio also promoted increased carbonation depths, although to a lesser extent. In Exposure Class 1, the 2 year depths of carbonation of the adjusted mixes were 1mm and 1.5mm higher than the Reference Mix and PC mix respectively. A study of the same mixes in an accelerated carbonation environment revealed a similar trend, as shown in Figure 6.3.

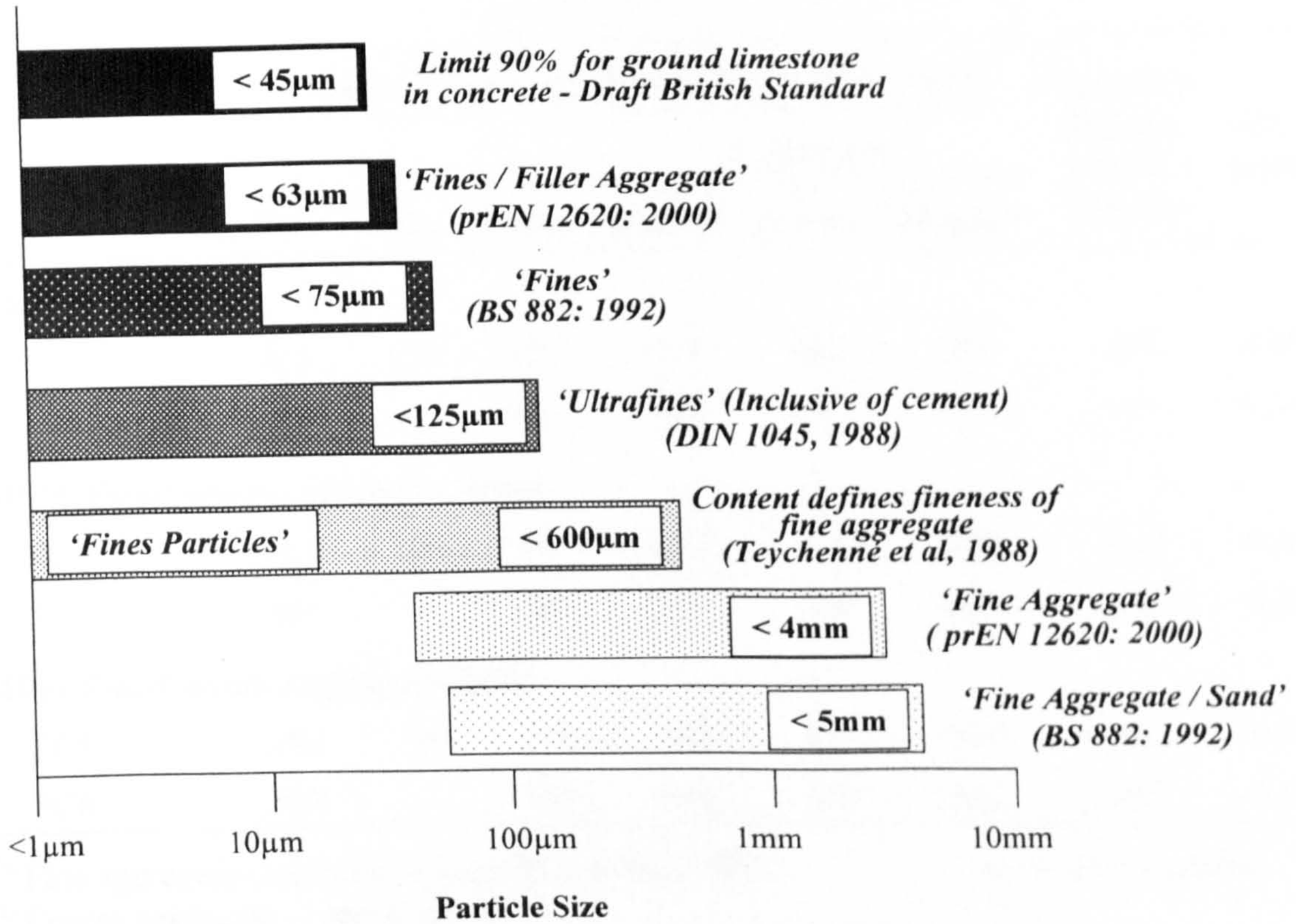


Figure 6.2 Definitions of 'fines' and fine aggregates given in various aggregate and concrete standards.

Table 6.3 Definition of fines as used on the current study.

Term	Definition
Fine Aggregate	Aggregate particles with a diameter of 5mm or less.
Fines	Particles less than 125µm *including* those from fine aggregate, cement and cement replacements such as PFA, MK and CSF.
Filler	Fine particles less than 45µm *excluding* cement or cement replacement such as PFA, MK and CSF.

Table 6.4 Mix proportions for Test Series 3 mixes normalised for $f_{cm,28}$ = 37N/mm².

Mix	Normalised Mix Constituent Proportions, kg/m³						Plasticiser Dosage, l/100kg Cement	w/c ratio
				Aggregates				
	PC	PFA	Water	Sand (1)	10 mm(2)	20 mm(2)		
Control Mixes								
FC1	265	110	170	640	400	800	nr*	0.46
FC2	300	-	185	700	400	800	nr*	0.59
+10% Fine/Coarse Aggregate Ratio								
FC3	265	110	170	820	340	680	0.35	0.46
FC4	300	-	185	855	350	695	0.30	0.59
-10% Fine/Coarse Aggregate Ratio								
FC5	265	110	170	460	460	920	nr*	0.46
FC6	300	-	185	490	470	940	nr*	0.59

(1) Fine aggregate conforms to Zone M, BS 882: 1992. nr* = none required
(2) Coarse aggregate - natural gravel.

Table 6.5 Fresh concrete characteristics and observations of Test Series 3 mixes.

Mix	Normalised Mix Constituent Proportions, kg/m³		
	Fine/Coarse Aggregate Ratio	Slump, mm	Comment on Fresh Concrete Appearance
Control Mixes			
FC1	0.35	70	Cohesive, uniform mix
FC2	0.35	75	Cohesive, uniform mix
+10% Fine/Coarse Aggregate Ratio			
FC3	0.45	60	Very cohesive mix
FC4	0.45	65	Cohesive mix
-10% Fine/Coarse Aggregate Ratio			
FC5	0.25	85	Harsh, open mix, some segregation
FC6	0.25	90	Harsh, open mix with segregation and bleeding

6.3.5 Chemical and Physical Characteristics of Test Series 3 Mixes

The total calcium hydroxide and permeation properties of the cover zone were examined prior to the specimens being placed in the CEN Test chamber. Table 6.6 shows that the total calcium hydroxide available in the outer 10mm was not substantially affected by adjusting the fine/coarse aggregate ratio. However, closer inspection of the permeation properties revealed that mixes with an increased and reduced fine/coarse aggregate ratio showed increased cover permeation compared to the control mixes.

The higher permeation properties led to an increased carbonation depth at 2 years, indicating the importance of the combined physical and chemical characteristics of the cover zone in resisting carbonation. The main concern was that increasing the total fines content by increasing the fine/coarse aggregate ratio was detrimental to the permeation properties and subsequent carbonation resistance of the hardened concrete. An increase in permeation properties was noted in the mixes having an increased fine/coarse aggregate ratio and was attributed to:

(i) Increased fines content. Maximum compaction was therefore more difficult to achieve.

(ii) Excess of fine material has increased the void ratio of fine and coarse aggregate leading to a reduced packing density of the concrete constituent materials.

A visual analysis of the concrete mixes did not support (i), as the plasticizing admixture dosage ensured a slump of 60-65mm for mixes FC3 and FC4. Therefore, the overall packing density and void ratio of the constituent materials was examined.

6.4 INVESTIGATION OF PACKING OF MIX CONSTITUENTS

6.4.1 Particle Size Distribution of Combined Concrete Mix Constituents

The relationship between the packing of concrete mix constituents and concrete microstructural properties can be traced back to 1892, when René Feret published an article on selecting the correct aggregate type in appropriate quantities for optimum concrete performance whilst relating the porosity of the hardened mortar to the concrete compressive strength (Josiel, 1952).

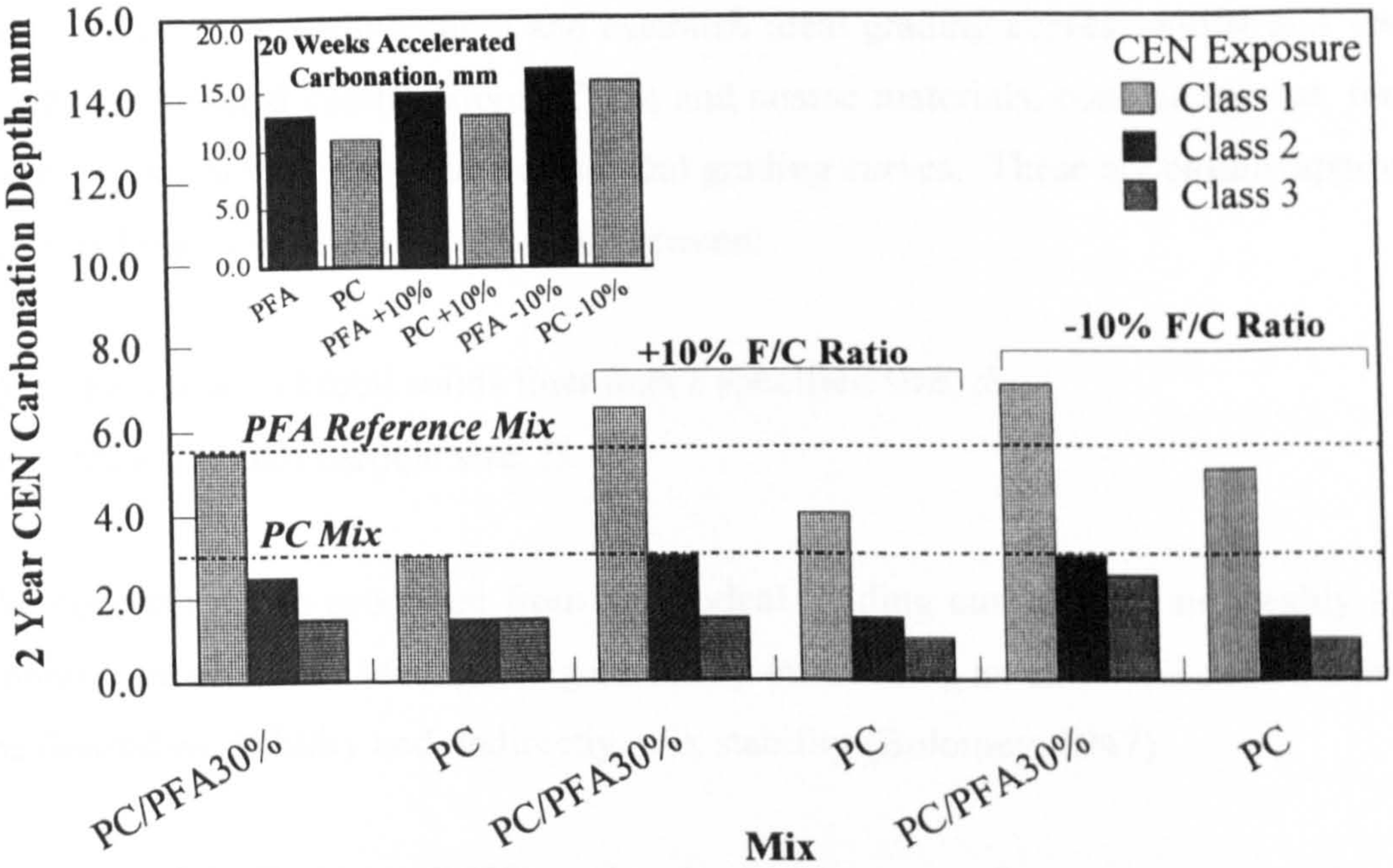


Figure 6.3 Comparison of 2 year CEN carbonation and 20 weeks accelerated carbonation of Test Series 3 mixes with adjusted fine/coarse aggregate ratios.

Table 6.6 Physical and chemical characteristics of Test Series 3 mixes prior to placement in the CEN Test chamber.

Mix	Pre-Entry Permeation Properties			
	WVD x 10^{-10} g/mm s Hg	**ISAT-10,** ml/m²/s x 10^{-2}	**Intrinsic Air Permeability,** m² x 10^{-17}	**Pre-Entry Total $Ca(OH)_2$,** % wt of cover zone concrete [1]
FC 1	112.0	55.4	35.0	1.7
FC 2	192.0	63.5	60.0	5.2
FC 3	119.5	58.9	40.5	1.7
FC 4	200.5	70.3	70.0	5.3
FC 5	125.5	86.6	46.6	1.8
FC 6	212.0	96.5	75.6	5.2

[1] Measured to a depth of 10mm

Early studies focussed on solving the problem of combining the fine and coarse aggregate to produce a desired grading curve and establish ideal grading curves. Fuller and Thompson (1907) investigated combinations of fine and coarse materials, concluding that, for certain combinations of materials, there exist ideal grading curves. These are closely approximated by a parabola by considering the ratio between:

(i) the fraction of total solids finer than a specified size, *d*;
(ii) the maximum particle size, *D*.

The concrete mixes produced from these ideal grading curves were noticeably harsh and Bolomey modified the ideal grading curves by introducing an empirical constant to consider the desired workability and, indirectly, mix stability (Bolomey, 1947).

Further work by Popovics (1993) lead to the development of an empirical equation:

$$P_t = f(d/D)^i + (1-f)(d/D)^h \qquad (6.1)$$

Where: P_t = fraction of total solids finer than size *d*
f = empirical constant
D = maximum particle size
i, h = empirical constants

The ideal grading curves proposed by Fuller and Thompson, and Bolomey, however, showed two basic weaknesses from a practical point of view (Day, 1995):

(i) it is rarely possible to replicate the gradings in the field;
(ii) the ideal grading for one use may not be simultaneously ideal for all uses.

Dewar also suggested that it would not be logical for the complex interaction of void filling and particle interference to lead to a single ideal particle size distribution of fine and coarse particles in concrete (Dewar, 1998). A number of researchers (Ehrenburg, 1980; Li and Ramakrishnan, 1983; De Larrard, 1988) have demonstrated advantages, such as improved workability as a result of gaps in the overall particle size distribution, however such mixes are recommended for specialised use only (Day, 1995).

6.4.2 Packing of Concrete Mix Constituents

The packing density of concrete depends on the choice of the particulate components, particle size, shape, and surface texture, as well as the overall mix proportions and mixing methodology (Powers, 1968).

A high packing density of a particulate mixture requires a broad distribution of particle sizes. Maximum packing is achieved only when the smaller particles fill the interstices between the larger particles without dilating the particle structure, and a typical binary mixture of spherical particles requires a volumetric ratio of 7:1 for effective packing to take place (Cumberland and Crawford, 1987). This may be explained by the fact that the triangular shaped pore formed by three closely packed spheres is approximately 1/6.5 of the largest sphere's diameter. A smaller size ratio, which is more common in a conventional PC concrete mix, is likely to induce some particle interference during the mixing stages. Therefore, the presence of much finer materials such as PFA or CSF can improve the packing density (De Larrard, 1988).

The random packing of mono-sized spherical particles was found to be consistent at 0.64 and 0.59 for dense and loose packing respectively (Scott, 1960). Many natural aggregates also show a relatively consistent packing density. For example, natural sand, with a relative density of 2.6 and loose bulk density of 1600kg/m^3, had a packing density of 0.62 (Dewar, 1986). However , the size of the particles has a major influence on packing. The surface area to volume ratio is indirectly proportional to the size of the particles, and so the effects of particle adhesion, surface friction, and capillary attraction become more significant (Murdock, 1960), and, in general, the packing density reduces with reducing particle size. A number of packing models have been developed and the most significant of these are summarised in Table 6.7.

6.4.3 Dewar Theory of Particulate Mixtures (1986, 1995)

The Dewar theory of particulate mixtures is based on work carried out by Powers and Brownyard (1948) and calculates packing for a large range of particle sizes including those less than 10μm. Further development of the model also led to the development of computer software for calculation of mix proportions to produce concrete with a minimum void ratio (Dewar, 1994). The principal of the model is based on the combination of fine and coarse particulate components and calculation of subsequent void ratio. The main assumptions of the model are as follow:

Table 6.7 Summary of common packing models for analysis of particulate mixtures.

Reference	Model	Parameters	Comments
Furnas, 1929	$\varphi_1 = \frac{a_1}{1-y_2} \quad \varphi_2 = \frac{a_2}{1-(1-a_2)y_1}$	Volume fraction ($y_{1,2}$) and packing densities ($a_{1,2}$) of binary components	Packing density (φ) only valid in large size ratioshence particle interference not accounted for.
Aim and Goff, 1967	$\varphi_1 = \frac{a_1}{1-y_2} \quad \varphi_2 = \frac{1}{\frac{y_2}{a_2} + (1-y).(1+0.9.\frac{d_2}{d_1})}$	Volume fraction ($y_{1,2}$) and packing densities ($a_{1,2}$) of components	Only accounts for 'wall effect' packing density (φ) of smaller particles packing against surface of larger particles.
Toufar et al, 1976	$\varphi = \frac{1}{[y_1/a_1 + y_2/a_2 - y_1.(1/a_1-1).k_d.k_s]}$	Bulk volume of coarse and fine particles(y_1/a_1, y_2/a_2), void volume of coarse particles $y_1(1/a_1-1)$, statistical factors (k_d, k_s)	Goltermann et al (1996) modified the model and developed Europack computer software package
Stovall et al, 1986	$\varphi = \frac{a_i}{1-(1-a_i)\sum_{j=1}^{i-1} g(i,j)y - \sum_{j=i+1}^{n} f(i,j)y_j}$	Eigenpacking of component *i* grains (a_i), loosening effect (f) and wall effect (g), determined theoretically and empirically	Can calculate multiparticle systems of any number of components. Considers loosening and wall effects. Relationship gives somewhat larger prediction than experimental values
Dewar, 1986, 1994	$U_0'' = (1+U_0)(1+mr)^3-1$ $Z = k_1 + [(1+U_0)^{1/3}-1-k_1]r^{k_2}$ $U_1'' = (1+U_1)U_0'' / [(1+U_0'') - (1+Z)^3)]-1$ $n = U_0''/(1+U_1''+U_0'')$ $U_n = y_2 U_1''$	Relative density, mean particle size and void ratio of each component (U), nominal width factor of voids (Z), volume of smaller particle fraction(n), m, k_1, k_2 are experimental constants	Combines components to achieve minimum voids ratio. Developed into MixSim 98 Software package for minimum void concrete mix design.

(i) Volume is a more relevant parameter than mass (or weight) for analysis;

(ii) Shape, surface texture and grading are accounted for by measuring the voidage of each particulate component;

(iii) In the vicinity of coarse particles the voidage of fine particles increases as their presence dilates the particle structure. This is termed 'particle interference';

(iv) All particles of any one component are assumed to be on one mean size.

Three fundamental parameters are required to characterise each particulate component:

(i) Relative Density = ρ;

(ii) Mean Particle Size = d_m (approximate sieve size at which 50% of the material passes);

(iii) Void Ratio = U (Void volume divided by the Solid Volume).

The void ratio for fine and coarse aggregate is determined experimentally in an unrodded state as this is more representative of the aggregate structure in compacted fresh concrete (Dewar, 1986). Finer materials, such as cement and filler, are characterised by means of water demand as determined by the Vicat test. The particulate packing model has four states as illustrated in Figure 6.4. The most complex state is the coarse particle dominant mixture, which is likely to produce a mixture with the minimum void ratio.

Figure 6.5 provides an example of the model, illustrated by means of a void ratio diagram. The lines U_0P and PU_1 represent the lower boundary of all possible binary mixture combinations. However, the presence of particle interference (loosening or the wall effect) means that the relationship between fine / coarse fraction and voids ratio will be similar to the line A, B, C, D, E, F, the exact relationship being dependent on the size ratio *r* (d/D) between the fine and coarse particles. The relationship between the fine/coarse particles and voids ratio is determined by the following steps:

i) Calculation of the effective void ratio for larger particle, U_0'';

ii) Calculation of the notional width factor for additional voids near coarse particles, *Z;*

iii) Determination of the effective void ratio for smaller particles, U_1'';

iv) Calculation of the smaller particle fraction, *n;*

v) Determination of the void ration, U_n.

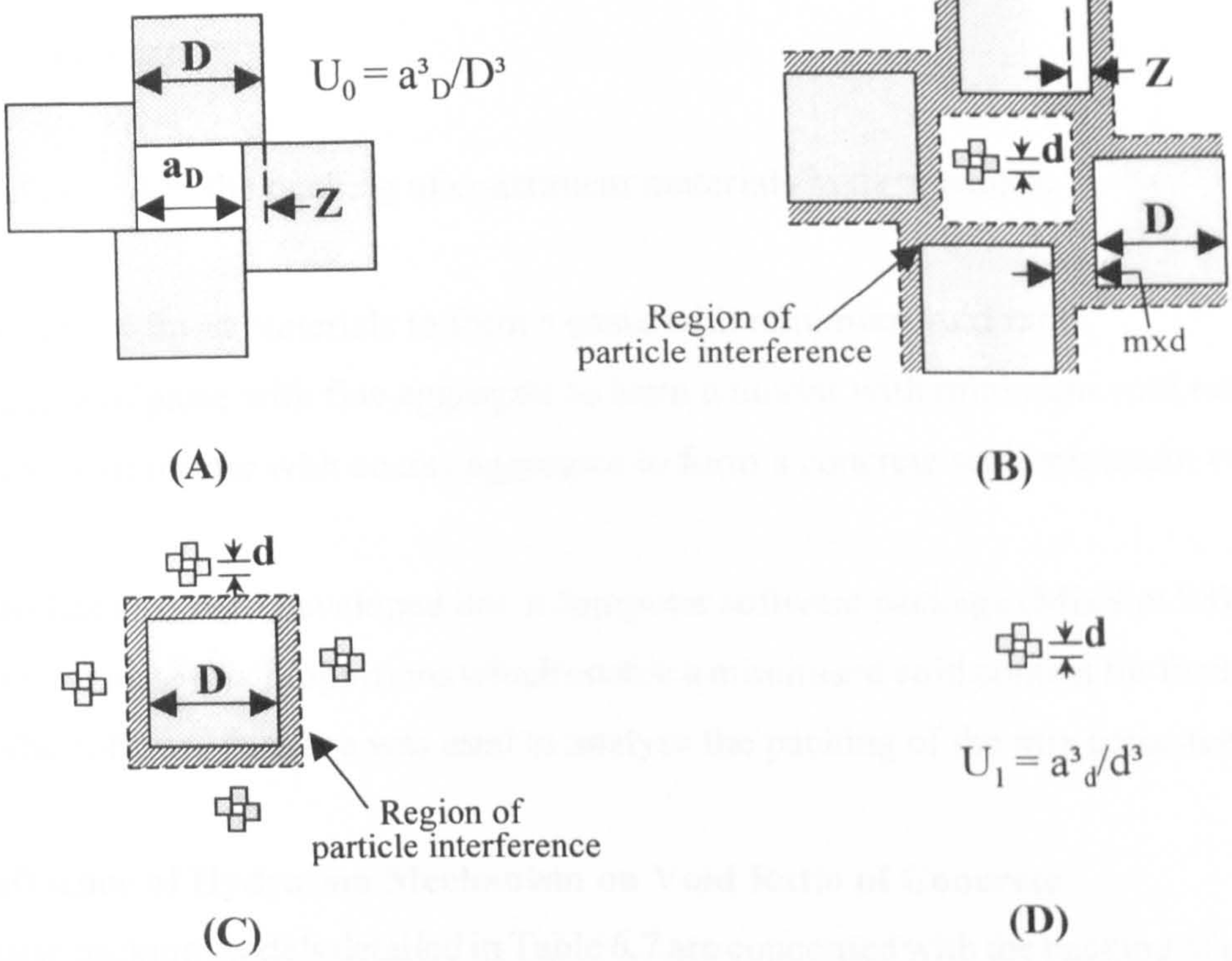


Figure 6.4 Four states of packing model (A) coarse particles only, (B) coarse particle dominant mixture, (C) fine particle dominant mixture (D) fine particles only (Dewar, 1994)

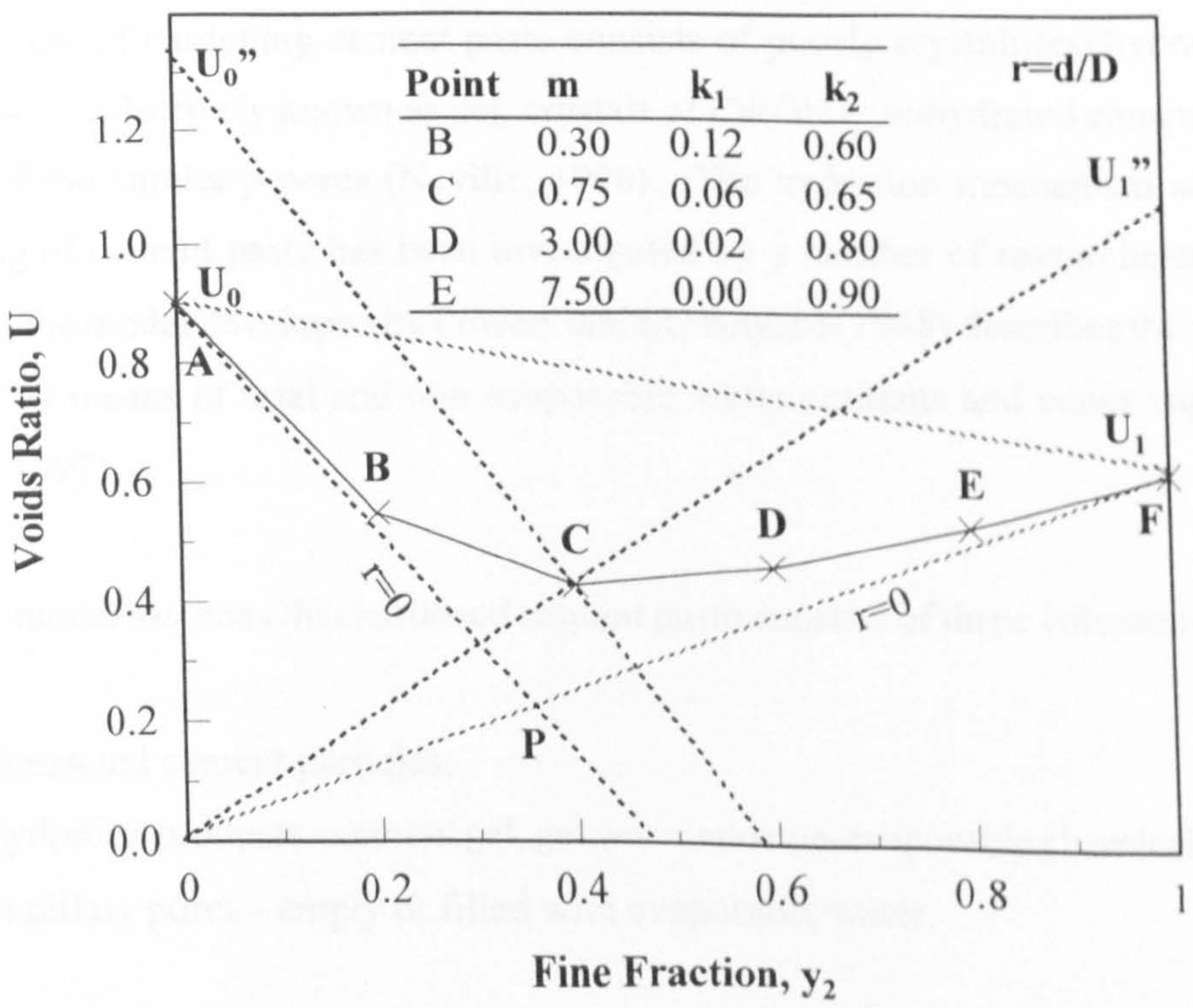


Figure 6.5 Dewar's Model illustrated by means of a void ratio diagram (After Dewar, 1994).

In determining the void ratio relationship, Dewar calibrated the constants, k_1, k_2 and m based on experimental data.

The model considers the packing of constituent materials in three stages:

i) Packing of finest materials to form a paste with minimum void ratio;
ii) Packing of paste with fine aggregate to form a mortar with minimum void ratio;
iii) Packing of mortar with coarse aggregate to form a concrete with minimum void ratio.

The model has also been developed into a computer software package (MixSim 98) allowing the user to calculate mix proportions which enable a minimised void content for fresh concrete mixes. The software package was used to analyse the packing of the mix constituents.

6.4.4 Influence of Hydration Mechanism on Void Ratio of Concrete

The particle packing models detailed in Table 6.7 are concerned with the packing of particulate materials which are in a steady state. However, this is only the case in concrete prior to or immediately when the water is added to the dry mixture. In reality, the chemical reaction between the cement and mix water means that the actual void ratio of concrete is a continuously changing parameter and is dependent on the degree of hydration (Taylor, 1997).

The structure of hardening cement paste consists of poorly crystallised hydrates of various compounds, collectively known as gel, crystals of $Ca(OH)_2$, unhydrated cement particles and residue of the capillary pores (Neville, 1996). The hydration mechanism and subsequent hardening of cement paste has been investigated by a number of researchers(Taylor 1997), however, the model developed by Powers and Brownyard (1948) describes the structure of the material by means of total and non-evaporable water contents and water vapour isotherms (Taylor, 1997).

Powers' model assumes that hardened cement paste consists of three volumetric components:

i) Unreacted cement particles;
ii) Hydration products - cement gel, gel water and non-evaporable chemically bound water;
iii) Capillary pores - empty or filled with evaporable water.

The porosity of the hardened cement paste is primarily a function of the capillary pores, although, the cement gel is also porous in nature (Powers and Brownyard, 1948). Given the average diameter of these gel pores (2-3nm), it is the capillary pores and the degree of hydration which will govern the overall void ratio of the hardened concrete (Powers and Brownyard, 1948; Taylor, 1997).

Powers and Brownyard (1948) stated that a water/cement ratio of at least 0.38 is required to enable full hydration of cement to take place under moist curing conditions, and under seal cured conditions, a water cement ratio of at least 0.44 is required for full hydration (Taylor, 1997).

The basis of the volumetric calculation of the structure of hardened Portland cement paste is as follows:

The total volume of paste (V_p)per unit mass of cement is

$$V_P = V_c + (w/c)/D_w \tag{6.2}$$

where V_c is the specific volume of cement, w/c is water/cement ratio and D_w is the density of the pore solution within the fresh paste.

The volume of the hydration products (V_{hp}) per unit mass of cement reacted is obtained by considering the degree of hydration of the cement:

$$V_{hp} = [V_c + (w/c^*)/D_w].\alpha \tag{6.3}$$

where w/c^* is the critical water/cement ratio which is required to achieve full hydration (assumed to be 0.38) and α is the degree of hydration.

The volume of unreacted cement particles (V_{uc}) per unit mass of cement at any given stage in the hydration process is determined by:

$$V_{uc} = V_c . (1-\alpha) \tag{6.4}$$

The specific volume of non-evaporable water (V_n) within the hydration products is determined by:

$$V_n = [(w/c^*)/D_w - V_g m_g]/m_n \quad (6.5)$$

where V_g is the mean specific volume of the gel water, assumed to be 1.00 x10^{-3} m³/kg, m_g is the mass of gel water, assumed to be α x 0.21, and m_n is the mass of non evaporable water which is assumed to be α x 0.23. In order to determine the porosity of the hydration product the ratio of the volume of the hydration product to the volume of the cement from which it was formed is calculated from:

$$V_{hp/c} = 1 + [(w/c^*)/(D_w \cdot V_c)] \quad (6.6)$$

The voids within the hydrated cementitious system are referred to here as the total porosity and may be split into two categories: the porosity of the hydrated gel; and the porosity of the system through the presence of capillary voids.

The gel porosity (P_{hp}) is expressed as a percentage of the total volume by

$$P_{hp} = V_g \cdot m_g \cdot \alpha/[V_c + (w/c)/D_w] \quad (6.7)$$

The quantity of gel pores is assumed to consist of those present in all hydration products, such as calcium-silicate-hydrates (C-S-H), calcium-aluminate-hydrates (C-A-H), and $Ca(OH)_2$ formed as a result of hydration. At full hydration, the porosity of cement gel was found to be in the region of 28% by volume (Powers and Brownyard, 1948), a figure which has been confirmed in a number of studies (Taylor, 1997).

The capillary porosity is dependent on both the water/cement ratio and degree of hydration, and can be expressed as a percentage of the total cementitious system by:

$$P_c = [w/c - \alpha(w/c^*)]/[(D_w \cdot V_c) + w/c] \quad (6.8)$$

As the hydration mechanism progresses, the volume of the gel and gel pores increases. This also leads to a reduction in the capillary porosity, as the hydration products occupy a greater volume than that of the initial cement and water (Taylor, 1997; Neville, 1996).

Figure 6.6 illustrates how the products of hydration and volume of capillary pores within a typical hydrating cementitious system are dependent on both the degree of hydration and the water/cement ratio. An illustrated example of the model developed by Powers and Brownyard is given in Figure 6.7. The Figure shows the gravimetric and volumetric proportions of a fully hydrated and saturated Portland cement paste with an initial water/cement ratio of 0.5. The 'total porosity' is given as a combination of the gel pores and capillary pores, however for the purpose of the current study, only the capillary pores will be considered for calculation of the potential void ratio of the hydrating concrete, since the capillaries are the governing factor in the permeation properties of the concrete, being approximately a single order of magnitude larger than the gel pores (Verbeck 1958).

The Powers-Brownyard model considers only the hydration of Portland cement pastes. For the purpose of the present study, the model has been slightly modified to take into account the effects of PFA, MK and CSF on the hydration characteristics of the hardened concrete. The pozzolanic reaction of PFA is assumed to take place after 28 days such that, at early ages, PFA acts in a similar manner to an inert filler, making little contribution to the hydration products although this depends on the physical and chemical characteristics of the PFA (Tittle, 1999). The reactivity of MK is known to take place at earlier ages in concrete (Wild and Khatib, 1997). The peak time for pozzolanic reactivity in concrete with up to 15% MK was found to be in the region of 7-14 days (Wild et al, 1996). The pH of expressed pore solution was also found to be reduced as early as 2 days, indicating that the MK was reacting with $Ca(OH)_2$ produced by hydration of the Portland cement (Coleman and Page, 1997).

The ultra-fine nature of CSF shows a similar reactivity to that of MK, with the peak pozzolanic reactivity occurring in the region of 7-14 days (Traettberg,1978, Cited Taylor, 1997). However, a number of studies have detected pozzolanic activity in CSF mixes occurring within hours, and, indeed, $Ca(OH)_2$ was being consumed after one day in some cases (Hjorth, 1982). The following assumptions were made in modifying the Powers-Brownyard model:

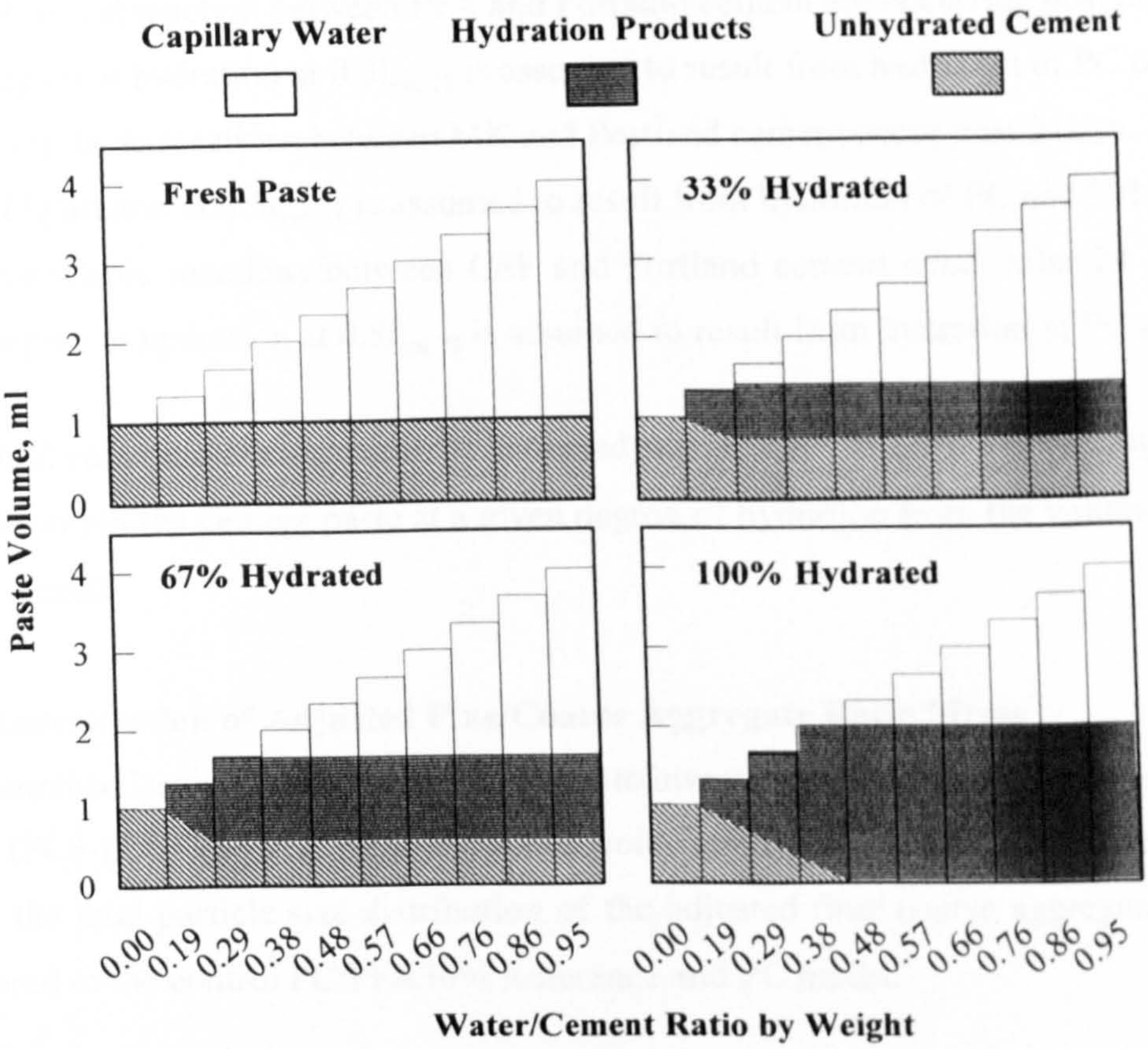


Figure 6.6 Composition of Portland cement paste at different stages of hydration (Powers, 1968).

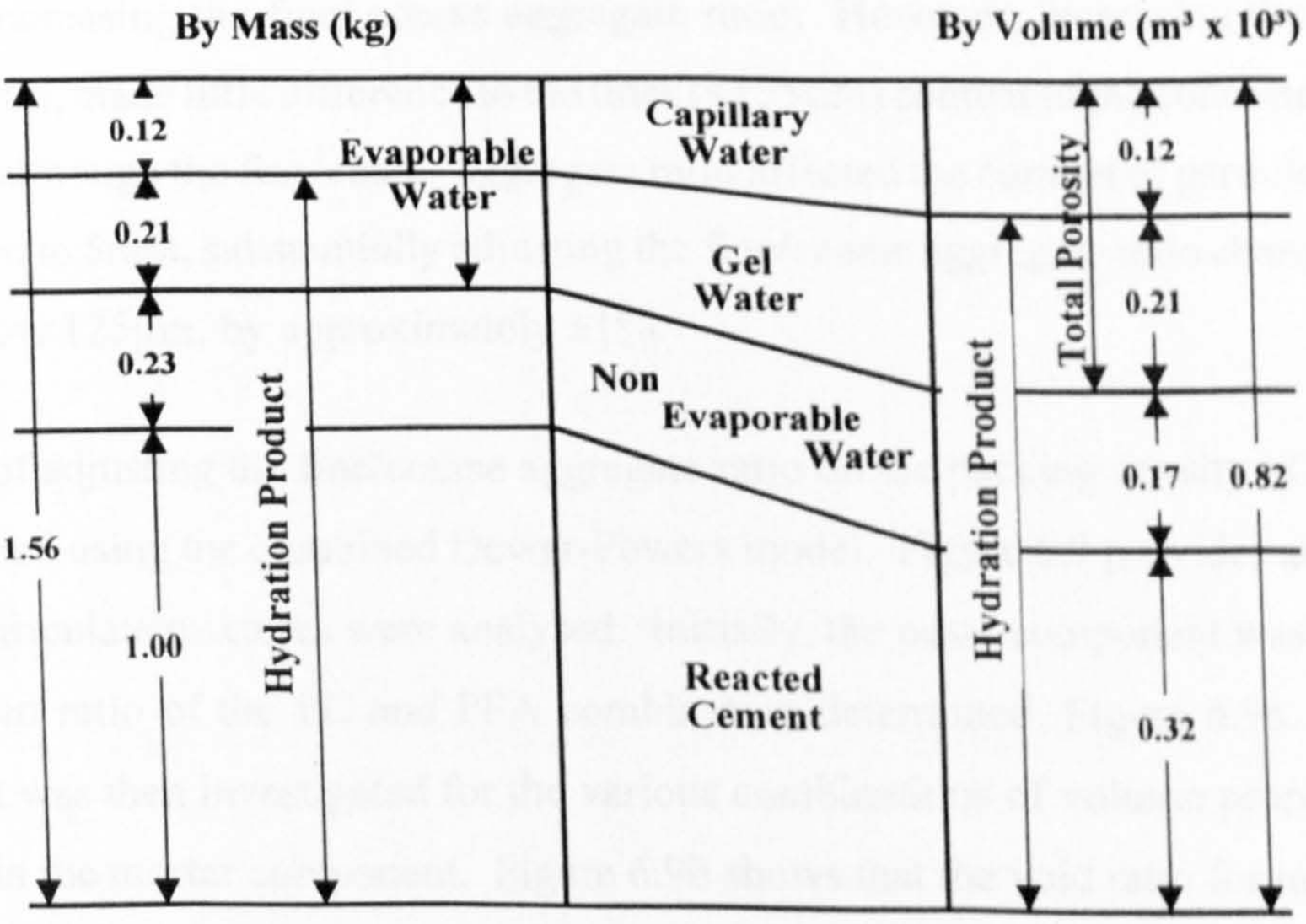


Figure 6.7 Illustration of the Powers-Brownyard description of a fully hydrated and saturated Portland cement paste of initial water/cement ratio 0.5. All quantities refer to 1kg of cement (Taylor, 1997).

(i) Chemical reaction between PFA and Portland cement are occurring post 28 days. The degree of hydration at $0.5f_{cm,28}$ is assumed to result from hydration of PC only;

(ii) Pozzolanic reactions between MK and Portland cement occur post 3 days. The degree of hydration at $0.5f_{cm,28}$ is assumed to result from hydration of PC and 50% of MK;

(iii) Pozzolanic reactions between CSF and Portland cement occur after 24 hours. The degree of hydration at $0.5f_{cm,28}$ is assumed to result from hydration of PC and CSF.

The actual void ratio of concrete in its hardened state is calculated by subtracting the volume of voids within the cement paste at a given degree of hydration from the volume of voids of fresh concrete.

6.4.5 Investigation of Adjusted Fine/Coarse Aggregate Ratio Mixes

The combined Dewar-Powers model was used to investigate the adjusted fine/coarse aggregate mixes (FC3-FC6) and determine the actual void ratio of the hardened concrete. Figure 6.8 shows the total particle size distribution of the adjusted fine/ coarse aggregate ratio mixes compared to the control PC/PFA30% Reference and PC mixes.

Increasing the fine/coarse aggregate ratio of the mixes reduces mean particle size of the constituent materials (in this case assumed to be D_{50}). The D_{50} of the PC/PFA30% Reference Mix was reduced from 4.0mm to 1.0mm, and D_{50} of the PC mix reduced from 4.2 mm to 1.7mm by increasing the fine/ coarse aggregate ratio. However, increasing the fine/coarse aggregate ratio, made little difference to the fines (<125μm) content of the concrete. Figure 6.8 shows that, although the fine/coarse aggregate ratio affected the content of particles within the range 600μm to 5mm, substantially adjusting the fine/coarse aggregate ratio changed the fines content below 125μm, by approximately ±1%.

The effect of adjusting the fine/coarse aggregate ratio on the packing density of the concrete was examined using the combined Dewar-Powers model. Figure 6.9 provides an example of how the particulate mixtures were analysed. Initially, the paste component was investigated and the void ratio of the PC and PFA combination determined, Figure 6.9a. The mortar component was then investigated for the various combinations of volume proportion, N_x, of paste within the mortar component. Figure 6.9b shows that the void ratio for mixes FC3 and FC5 (± 10% fine/coarse aggregate ratio) were the same. Even at this stage of the analysis, it was apparent that adjusting the fine/coarse aggregate ratio was having a detrimental effect on the packing of the constituent materials, the optimum paste/mortar ratio in this case being in the region of 0.4.

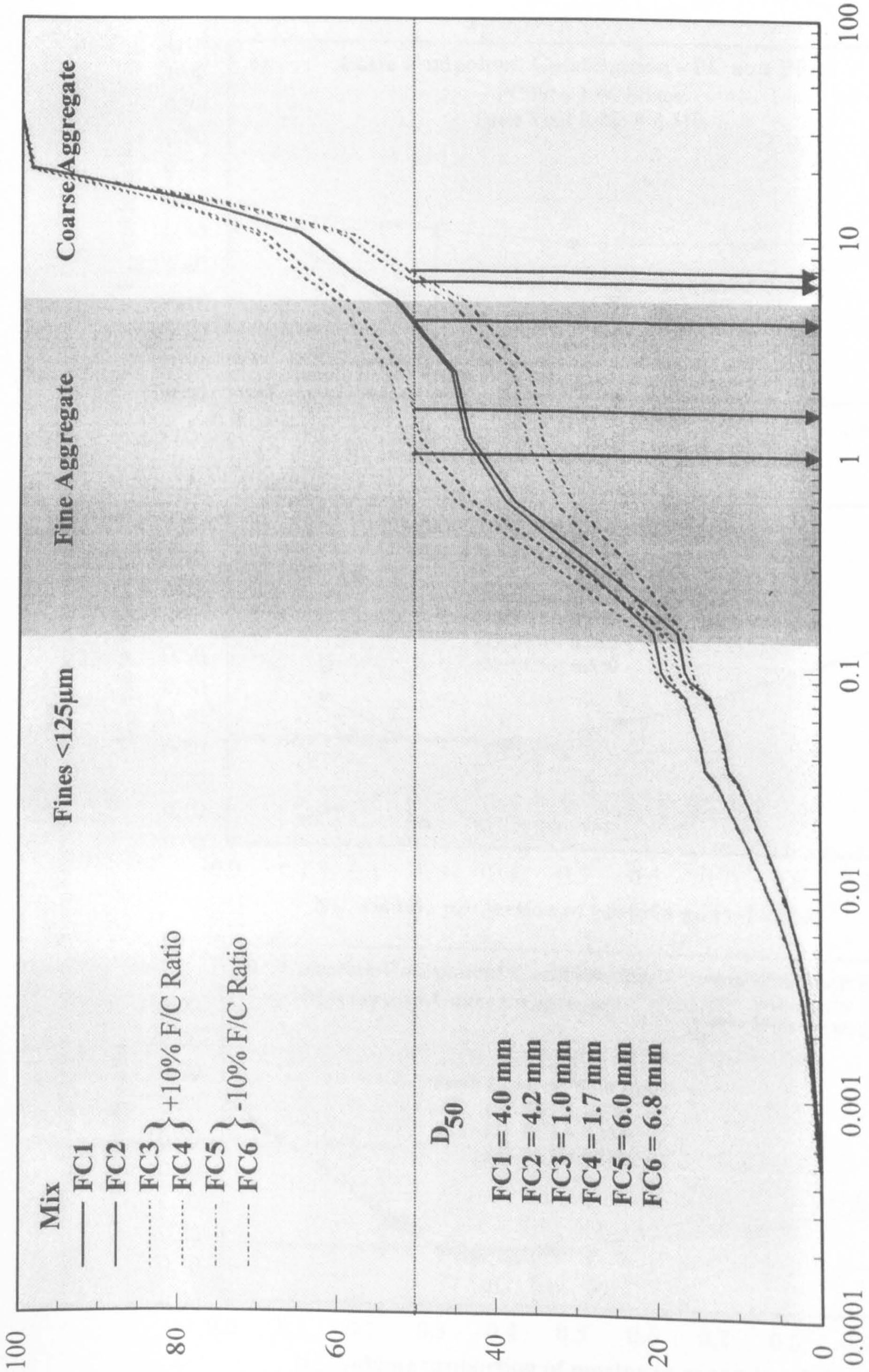


Figure 6.8 Overall particle size distribution of Test Series 3 Mixes showing D_{50} for each mix.

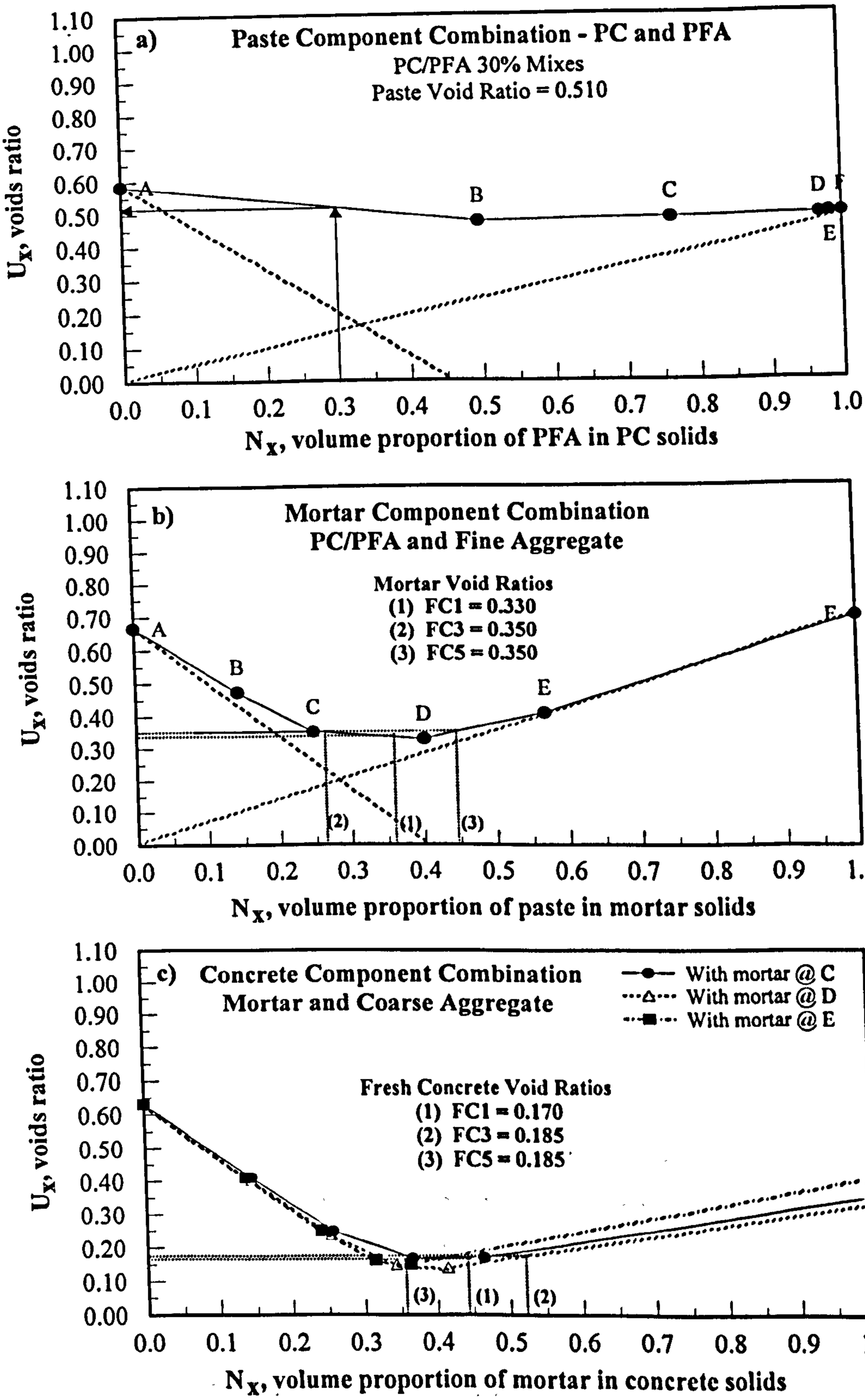


Figure 6.9 Example of analysis of constituent material packing of PC/PFA30% concrete with adjusted fine/coarse aggregate ratio.

To analyse the packing of all mix constituents for Mixes FC1, FC3 and FC5, theoretical concrete mixes designed with mortars of paste/mortar ratios 0.25, 0.40 and 0.55 were investigated. Figure 6.9c shows that mix FC1 had the lowest void ratio compared to mixes FC3 and FC5, again indicating that simply adjusting the fine/coarse aggregate content is not sufficient to improve the packing density of concrete.

The true voids ratio of concrete prior to exposure to an aggressive environment will also be a function of its curing and degree of hydration. The formation of hydration products with a greater volume than the combined initial cement and water will reduce the capillary voidage of the concrete (Taylor, 1997), thereby reducing the overall void ratio of the hardened mix. Figure 6.10 gives an example of the hydration mechanism calculation for the PC/PFA30% Reference Mix, seal cured until $0.5f_{cm,28}$ was reached. The measured degree of hydration, α, was 0.59. The initial void ratio of the fresh paste was determined as 0.510, and the void ratio of the hardened paste was determined as 0.501, a reduction of 0.009 due to the formation of hydration products. This reduction in the paste component was then applied to the overall concrete void ratio giving an actual concrete void ratio of 0.166.

Table 6.8 compares the void ratios (U_x) and packing densities (φ_f, φ_h) of the fresh and hardened concrete in Test Series 3 mixes. Mixes FC3 and FC4 with increased fine/coarse aggregate ratios exhibited higher void ratios and lower packing densities compared to the control mixes. As expected, the mixes with reduced fine/coarse aggregate ratios had a reduced packing density, and this was reflected in the 2 year CEN and 20 weeks accelerated carbonation depths.

The increased void ratios in mixes FC3 and FC4 were attributed to two phenomena:

i) The larger content of particles in the region 300 μm to 600μm was increasing the possibility of particle interference. The 'loosening effect', whereby an excess of finer particles in a binary mixture can cause the displacement of larger particles, may be occurring;

ii) The wall effect at the coarse aggregate interface may also be occurring due to the larger content of particles in the region of >600μm. Poorer packing of mortar around the coarse aggregate will lead to an increase in voids. This is reflected in the increased permeation properties of the mixes.

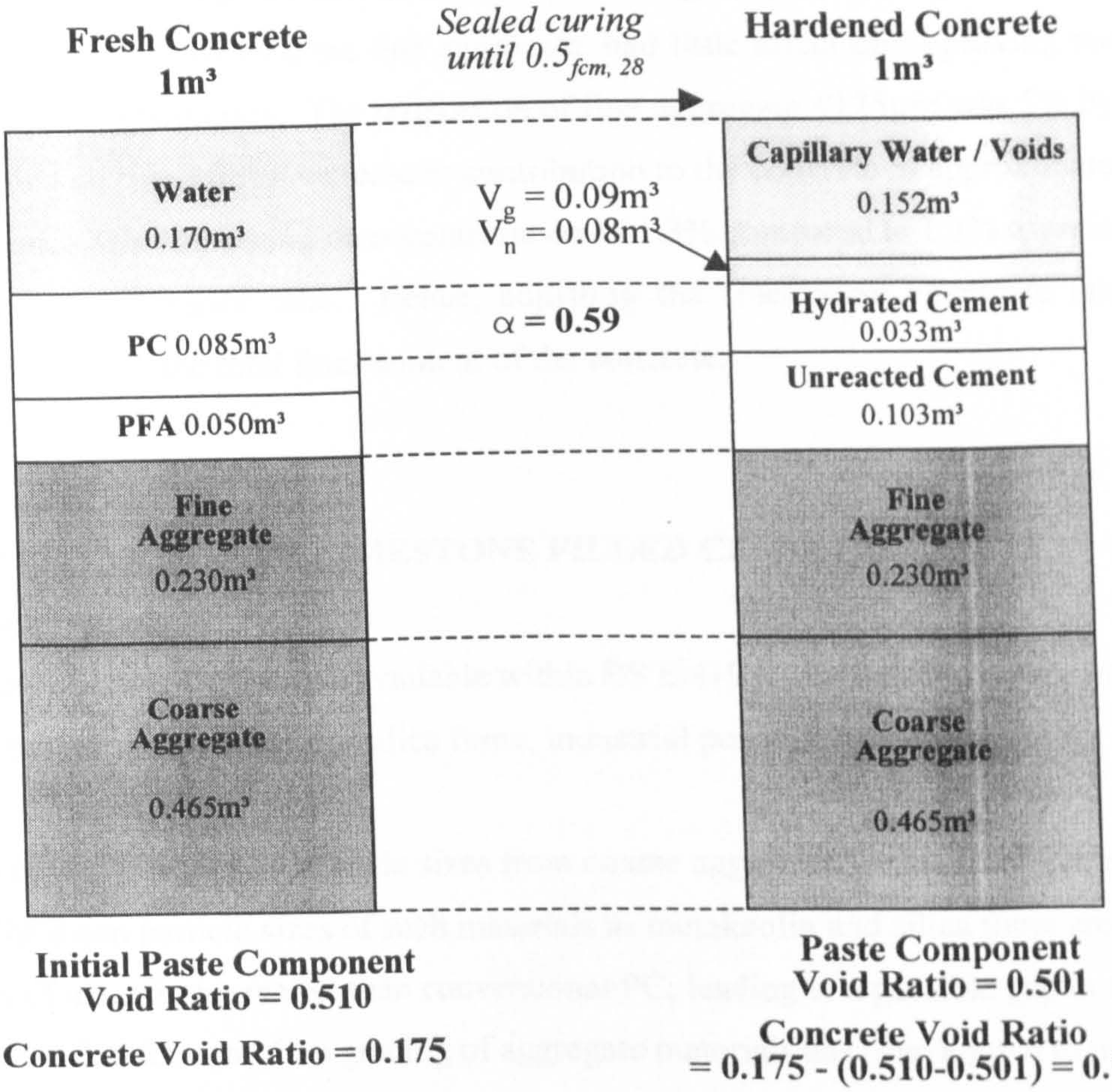


Figure 6.10 Example of volumetric calculation of actual void ratio of hardened concrete after seal curing until $0.5f_{cm,\,28}$ is reached for PC/PFA30% Reference Mix.

Table 6.8 Comparison of void ratio, U_x, packing densities, φ, and carbonation depths of Test Series 3 mixes.

Mix	Fresh Concrete		Hardened Concrete at $0.5f_{cm,\,28}$		Depth of Carbonation, mm	
	U_x	φ_f [1]	U_x	φ_h [1]	20 Weeks [2]	2 Years [3]
FC1	0.175	0.851	0.166	0.858	13.0	5.5
FC2	0.183	0.845	0.172	0.853	11.0	3.0
FC3	0.180	0.847	0.171	0.854	15.0	6.5
FC4	0.195	0.837	0.184	0.844	13.0	4.0
FC5	0.199	0.834	0.190	0.840	17.0	7.0
FC6	0.200	0.833	0.189	0.841	16.0	5.0

[1] Packing Density $\varphi = 1/(1+U_x)$ [2] Accelerated Carbonation [3] CEN Carbonation Class 1

It was clear from the Test Series 3 mixes that increasing the proportion of material within a certain size band, in this case the fine aggregate, had little effect on improving the overall packing of mix constituents. The proportion of fine aggregate <125μm was 5% by weight, giving an overall 'sand fines' increase in contribution to the concrete of approximately 0.4%. The Reference Mix had a sand fines contribution of 1.3% compared to 1.7% from increasing the fine/coarse aggregate ratio. Hence, adjusting the fine/coarse aggregate ratio had a negligible effect on the total fines content of the concrete.

6.5 CARBONATION OF LIMESTONE FILLED CEM II CONCRETE

6.5.1 Background

The variety of cement types now available within BS EN197-1 include the composition of PC and fine particle binders such as silica fume, industrial pozzolanas and limestone.

In many cases, the range in particle sizes from coarse aggregate to the finest cement is very wide. The mean particle sizes of such materials as metakaolin and silica fume are a number of orders of magnitude smaller than conventional PC, leading to a possible gap in the overall particle size distribution. Gap grading of aggregate materials has been known to increase the void content of concrete. However, the current study investigates the effect of ultrafine cements on the void ratio and packing density of concrete, and attempts to improve the packing density by bridging the gap between ultrafine particles and typical cement sized particles.

6.5.2 Improving the Packing Density of CEM II Concrete

The mixes tested in Series 1 were examined to determine the packing density using the combined Dewar-Powers-Brownyard model. From the investigation of Test Series 3 mixes, the influence of the paste content in the mortar component was substantial, hence the current part of the study focussed on minimising the paste and mortar void ratio. Figure 6.11 details the relationship between the volume fraction of paste in the mortar component, N_x, and the void ratio of the mixture, U_x. The example shown for the CSF 10% mix shows the paste to mortar ratio having an N_x of 0.262, however the void ratio diagram shows that the optimum N_x to achieve the minimum void ratio would be 0.400. For the case of the CSF 10% mix, the mortar void ratio would potentially be reduced from 0.420 to 0.352, representing an increase in packing density of 4%. This was found to be the case in all CEM II concretes in the current study, with an increase in N_x for the paste/mortar ratio required to achieve the minimum mortar void ratio and maximum packing density.

The paste/mortar ratio of the mixes may be increased by reducing the volume fraction of the fine aggregate, and replacing this with cement, however, this gives rise to two concerns:

i) Increasing the cement content of the concrete may not be economically viable;
ii) Adjusting the fine/coarse aggregate ratio of the mix may be detrimental to the permeation properties and carbonation resistance of the hardened concrete.

A fine aggregate replacement method was investigated whereby a volume fraction of the fine aggregate was replaced with a volume fraction of limestone filler, the principal of which is shown in Figure 6.12. The D_{50} of the limestone filler was such that the material was in the size range between that of the cement particles (D_{50} = 15μm) and the finer materials, such as PFA (D_{50} = 9μm) CSF (D_{50} = <1μm) or MK (D_{50} = 2μm).

Fine limestone can be used as both a filler material and considered as part of the cementitious matrix. However, the current study considers the material purely as a filler. The limestone is considered part of the paste component only from the instance that it is physically influencing the packing of the paste materials, and having no chemical influence on the hydration of the paste.

6.5.3 Test Series 4 Mixes: Limestone-filled CEM II Concrete

To determine the effect of partial replacement of fine aggregate with limestone filler, a series of mixes were developed with limestone replacement levels of 5%, 10%, 15% and 20% by weight of fine aggregate. The mix designs are given in Chapter 3. In most cases, the mixes with limestone replacement required a dosage of plasticizing admixture to obtain the required workability of slump class S2 (60-90mm) in BS EN 206-1. Compressive strength testing showed that the effect of replacing a proportion of the fine aggregate with limestone filler had a negligible effect on the 28 day compressive strength for all mixes designed to 37N/mm².

Table 6.9 gives details of the fines content, void ratios, and packing densities of the fresh and hardened concrete, and carbonation performance of Test Series 4 mixes. In all cases, increasing the replacement level of limestone filler increased the fines content of the mixes. As the fines content included all materials less than 125μm, inclusive of cement, the PC/PFA30% Reference Mix had the largest overall fines content due to a higher cement content being required to achieve the design strength of 37N/mm². The CSF and MK mixes had the lowest fines content, compared on replacement level, as the initial cement contents of these mixes were lower than the Reference Mix.

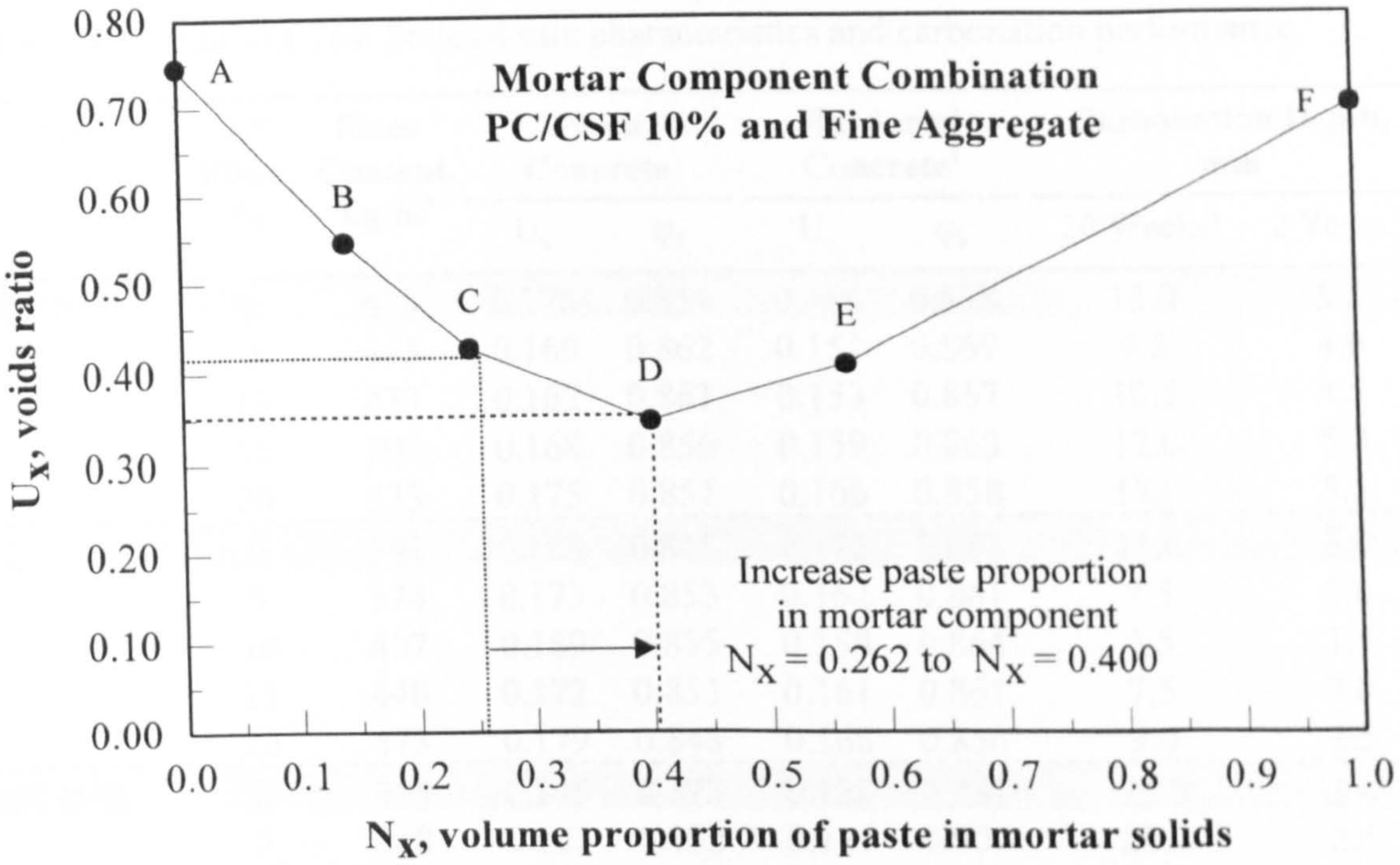


Figure 6.11 Investigation of mortar component of CSF 10% CEM II concrete.

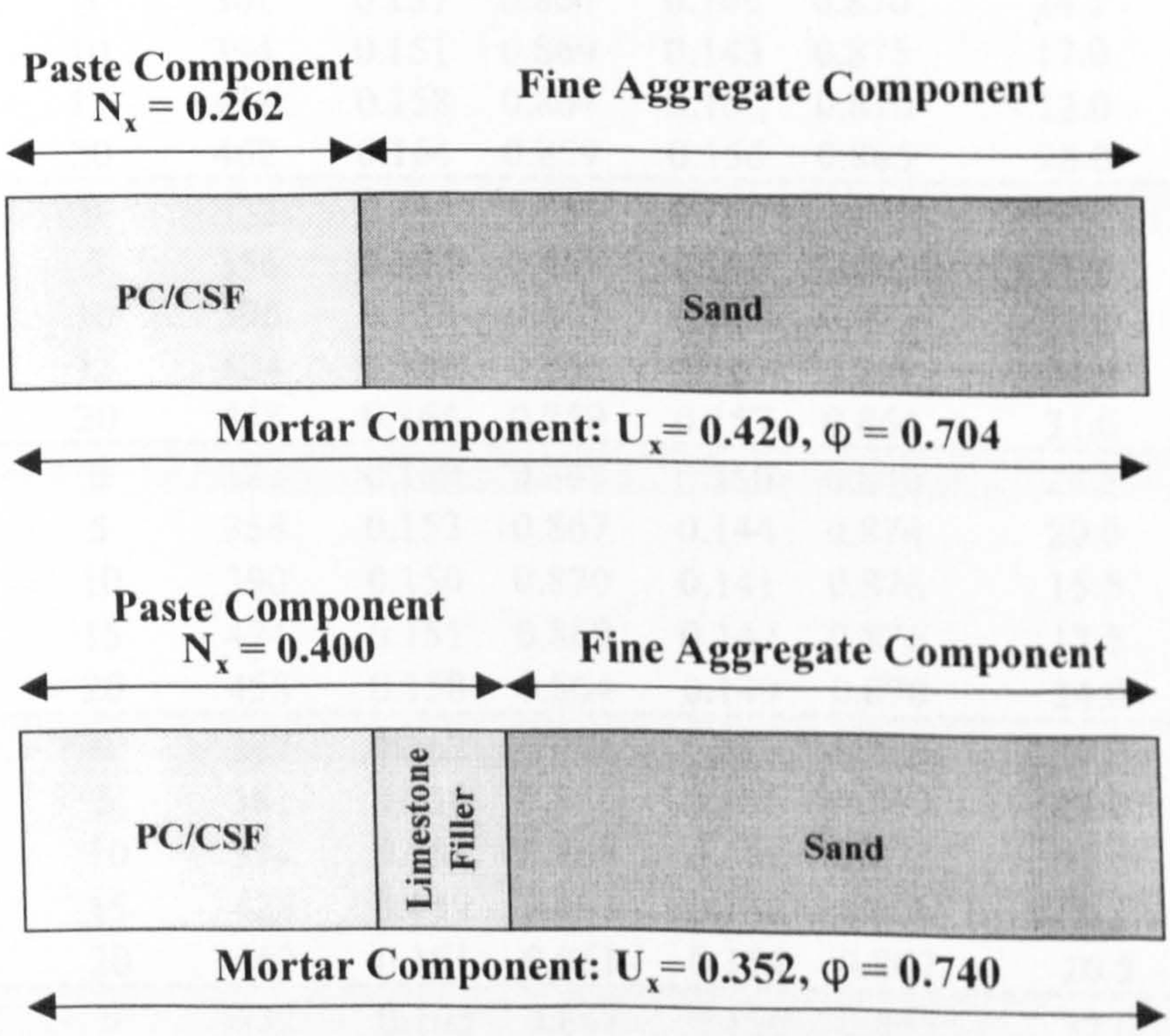


Figure 6.12 Principle of increasing paste component in mortar component of PC/PFA30% concrete by replacing a volume fraction of the fine aggregate with limestone filler.

Table 6.9 Details of Test Series 4 mix characteristics and carbonation performance.

Mix	LS Filler, %	Fines [1] Content, kg/m³	Fresh Concrete		Hardened Concrete[2]		Carbonation Depth, mm	
			U_x	φ_f	U_x	φ_h	20 Weeks[3]	2 Years [4]
PC/PFA	0	413	0.175	0.851	0.166	0.858	13.0	5.5
	5	443	0.160	0.862	0.151	0.869	9.5	4.0
	10	473	0.162	0.861	0.153	0.867	10.5	4.5
	15	503	0.168	0.856	0.159	0.863	12.0	5.0
	20	533	0.175	0.851	0.166	0.858	13.0	5.5
PC	0	341	0.183	0.845	0.172	0.853	11.0	3.0
	5	374	0.173	0.853	0.162	0.861	7.5	2.0
	10	407	0.169	0.855	0.158	0.864	5.5	1.5
	15	440	0.172	0.853	0.161	0.861	7.5	2.0
	20	473	0.179	0.848	0.168	0.856	9.0	2.5
MK 10%	0	355	0,145	0.873	0,135	0.881	25.0	3.0
	5	388	0.121	0.892	0.111	0.900	20.0	2.5
	10	420	0.120	0.893	0.110	0.901	18.0	2.5
	15	452	0.128	0.887	0.118	0.894	24.0	3.0
	20	484	0.150	0.870	0.140	0.877	27.0	4.0
MK 15%	0	327	0.162	0.861	0.154	0.867	29.0	6.0
	5	361	0.157	0.864	0.149	0.870	24.5	5.0
	10	394	0.151	0.869	0.143	0.875	17.0	4.0
	15	428	0.158	0.864	0.150	0.870	22.0	5.0
	20	462	0.164	0.859	0.156	0.865	26.0	6.5
MK 20%	0	322	0,166	0.858	0,159	0.863	33.0	7.5
	5	356	0.162	0.861	0.155	0.866	25.5	6.0
	10	390	0.153	0.867	0.146	0.873	21.0	5.0
	15	424	0.160	0.862	0.153	0.867	23.0	5.5
	20	458	0.164	0.859	0.157	0.864	31.0	7.0
CSF 10%	0	322	0.159	0.863	0.150	0.870	24.5	6.5
	5	356	0.153	0.867	0.144	0.874	20.0	5.5
	10	390	0.150	0.870	0.141	0.876	15.5	4.5
	15	424	0.151	0.869	0.142	0.876	17.5	5.0
	20	458	0.158	0.864	0.149	0.870	24.0	6.5
CSF 15%	0	327	0.162	0.861	0.155	0.866	27.0	7.0
	5	361	0.158	0.864	0.151	0.869	21.0	5.5
	10	394	0.152	0.868	0.145	0.873	17.5	4.5
	15	428	0.159	0.863	0.152	0.868	20.5	5.5
	20	462	0.161	0.861	0.154	0.867	26.5	6.5
CSF 20%	0	332	0,165	0.858	0,156	0.865	32.0	7.5
	5	365	0.160	0.862	0.151	0.869	27.5	6.0
	10	399	0.156	0.865	0.147	0.872	22.0	5.5
	15	432	0.160	0.862	0.151	0.869	27.0	6.0
	20	466	0.164	0.859	0.155	0.866	32.0	7.0

[1] All particles <125μm. [2] At $0.5f_{cm,28}$ [3] Accelerated Carbonation [4] CEN Exposure Class 1

The partial replacement of fine aggregate with limestone filler also reduced the concrete void ratio in most cases. However, closer inspection shows that, depending on the mix type, there appears to be an optimum level of replacement and total fines content to achieve a minimum void ratio and maximum packing density. The PC/PFA30% Reference Mix had a maximum packing density when 5% of the fine aggregate was replaced with limestone filler, corresponding to a fines content of 443kg/m^3. However, the CEM I and remaining CEM II concretes showed a minimum voids ratio and maximum packing density at a limestone - fine aggregate replacement level of 10%. In the CEM II concretes this corresponded to a fines content in the region of 390kg/m^3.

The corresponding carbonation performance of Test Series 4 mixes was reflected in the fresh and hardened concrete void ratios and packing densities, Table 6.9. After both 20 weeks accelerated and 2 years CEN carbonation, the lowest depths of carbonation were recorded in those mixes having the lowest void ratios and highest packing densities, indicating that consideration of the physical material properties is vital in carbonation resistance.

The reduced packing densities and poorer carbonation performance in mixes with higher fines contents were attributed to the particle interference phenomenon observed in Test Series 3 mixes, in particular the loosening effect associated with an excess of fine materials in a binary particulate mixture (Dewar, 1986).

The relationship between fines content, packing density, and 2 year CEN carbonation depth in CEM II concrete is more clearly illustrated by means of a surface plot shown in Figure 6.13. The Figure shows that for CEM II concrete, an optimum fines level, to obtain a maximum packing density, is visible in the region of 390-400kg/m^3. This optimum level of fines is more prevalent in concretes with a higher packing density, as the 2 year CEN carbonation depths are markedly reduced, indicating that the range of particle sizes and overall particle size distribution of constituent materials may be approaching some form of 'ideal grading' to ensure minimum voids.

The permeation properties of the limestone filled concretes were also examined by means of ISAT-10, intrinsic air permeability, and water vapour diffusivity tests. Figures 6.14, 6.15 and 6.16 indicate the relationship between the fines content and 2 year carbonation depth, and pre-entry ISAT-10, intrinsic air permeability, and water vapour diffusivity respectively. In all cases, the relationship between the permeation property, fines content and 2 year carbonation

depth shows a trend towards an optimum fines content in the region of 390-400kg/m^3. The relationship between fines, carbonation and ISAT-10 is somewhat less obvious than the other permeation properties. This was attributed to the fact that the carbonation process is more likely to be directly influenced by the concrete permeability and diffusivity properties rather than its absorptive properties (Richardson, 1988).

It is interesting to note that the reduction in permeation properties associated with the inclusion of the filler material were similar to the permeation requirements found using the sensitivity analysis in Chapter 5 to achieve similar performance to the PC/PFA30% Reference Mix. To achieve a similar performance to that of the PC/PFA30% Reference Mix, the CSF 10% mix, for example, required a 30% reduction in ISAT-10, and this was achieved through a 10% replacement of the fine aggregate with limestone filler. This was also found to be the case in most of the CEM II concretes. However, in some cases, a greater reduction in permeation properties was achieved at the optimum fines content, thus giving a better performance than the PC/PFA30% Reference Mix.

CEN proposed a minimum fines content of 330kg/m^3 for concrete in a carbonating environment (CEN, 1997). This limit is based on the requirements of the German structural concrete standard DIN 1045 (DIN, 1988). However, from the current study, the fines content can heavily influence the packing density, permeation properties, and subsequent carbonation performance of concrete, and this is dependent on a number of factors such as material physical properties, mix proportions, and concrete designation.

For the CEM II concretes in the present study, an optimum fines content of 395 ± 5kg/m^3 is proposed to ensure that, within a given concrete grade, the permeation properties are sufficiently low to provide adequate carbonation resistance through physical modification of the concrete pore structure.

6.5.4 Chemical Influence of Limestone of CEM II Concrete

The inclusion of limestone filler in CEM II concrete improved the carbonation resistance by modifiying the pore structure of the concrete and reducing the permeation properties.Given the chemical nature of limestone filler, which is predominantly calcium carbonate, the cover zone chemistry was examined to determine the effect of including limestone in the concrete. The inclusion of a carbonate within the cover zone had the potential to influence the cover zone chemistry and hydration mechanisms of the hardening concrete.

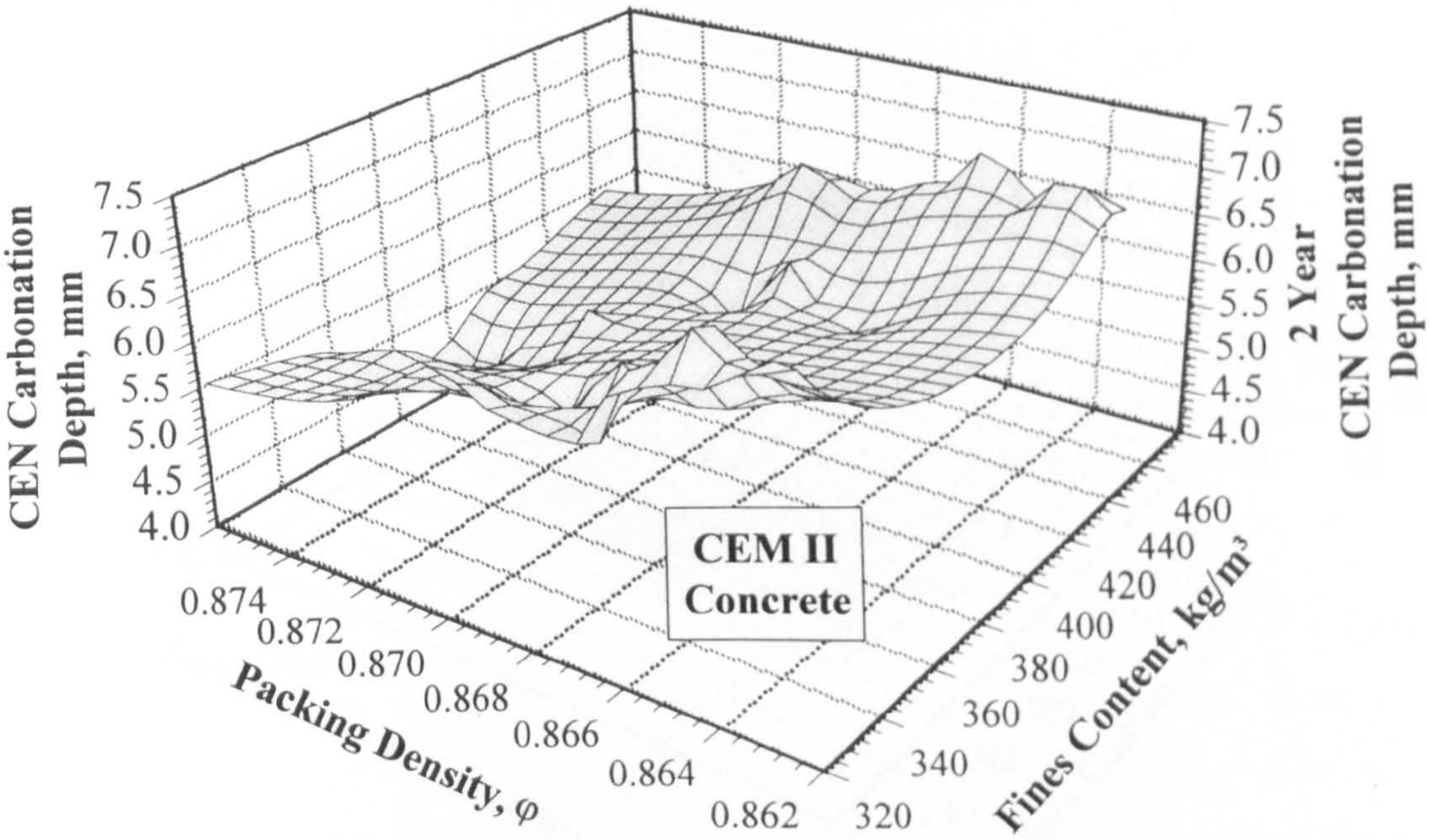


Figure 6.13 Relationship between fines content, packing density, and 2 year CEN carbonation for CEM II concretes.

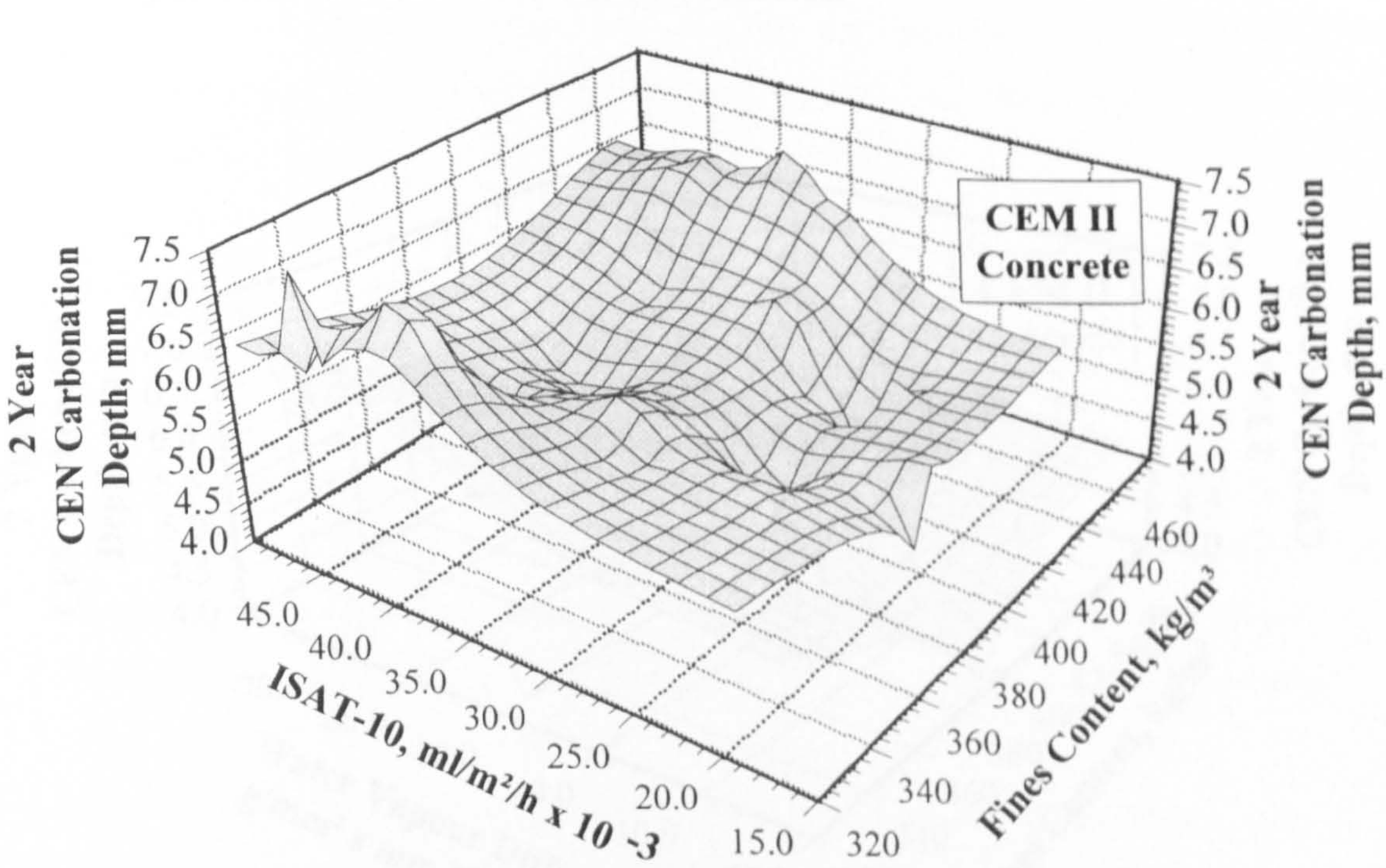


Figure 6.14 Relationship between fines content, pre-entry ISAT-10, and 2 year CEN carbonation for CEM II concretes.

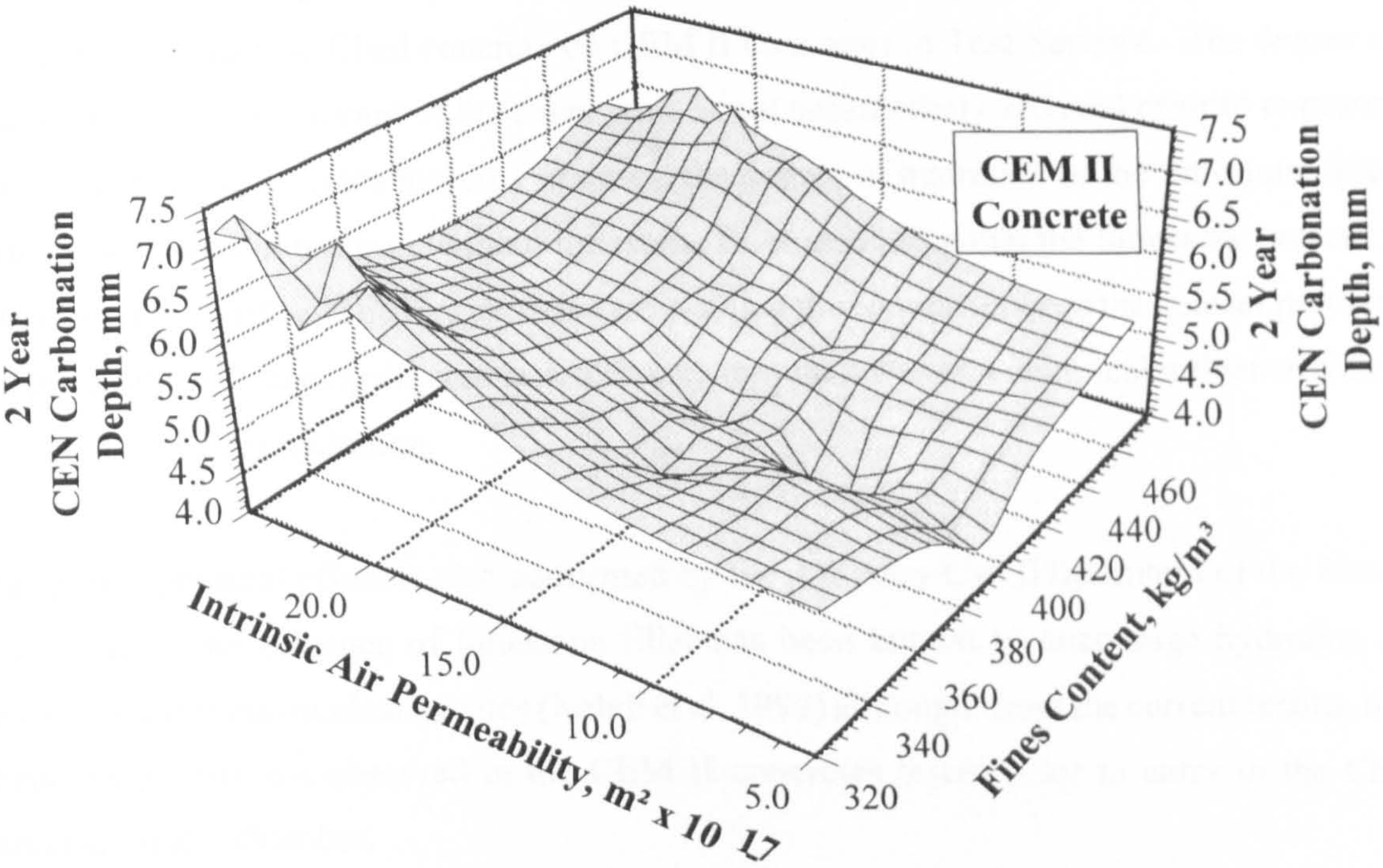


Figure 6.15 Relationship between fines content, pre-entry intrinsic air permeability, and 2 year CEN carbonation for CEM II concretes.

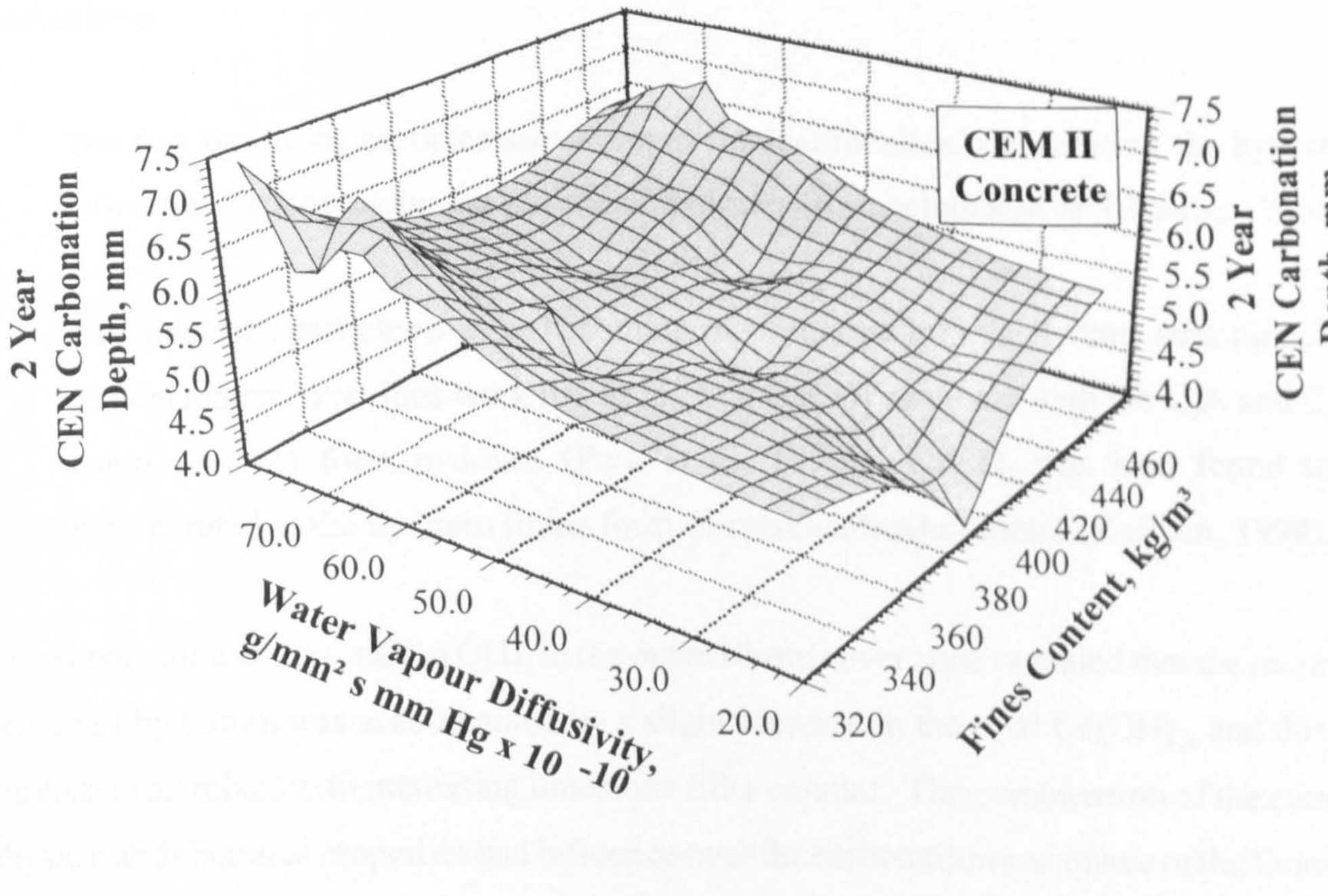


Figure 6.16 Relationship between fines content, pre-entry water vapour diffusivity, and 2 year CEN carbonation for CEM II concretes.

Table 6.10 gives the degree of hydration and total calcium hydroxide measured within the outer 10mm of the limestone filled concrete on CEM II concretes in Test Series 4. The degree of hydration in the outer 10mm of the cover zone is not substantially affected prior to exposure to CEN carbonation. In the majority of cases, the degree of hydration of the limestone filled mixes is very similar to those without limestone filler indicating that the limestone present is acting purely as a filler. The fine particles are packing the spaces between the coarser particles and physically influencing the concrete, although they do not exert a chemical influence within the first 3-4 days of hydration.

This purely physical effect is also confirmed by the pre-entry $Ca(OH)_2$ content of the 10mm cover zone. The presence of limestone filler has been known to encourage hydration by providing additional nucleation sites (Nehdi et al, 1998) although, from the current results, this phenomenon was not observed in the CEM II concretes tested prior to entry to the CEN carbonation test chamber.

After a period of 2 years, the degree of hydration was affected by the presence of limestone within the mix. Mixes with increasing levels of limestone filler showed an increased degree of hydration at a period of 2 years. The presence of limestone in the concrete appeared to be chemically influencing the hydration mechanism and this was attributed to two possible mechanisms:

i) The fine limestone particles are acting as nucleation sites, accelerating the hydration process and encouraging the growth of hydrates (Ramachandran and Zhang, 1986);

ii) The limestone particles may be becoming incorporated into the hydrate structure of the cement matrix. Previous work has found that $CaCO_3$ can react with the C_3A and C_4AF components to form hydrates (Pera et al, 1999). $CaCO_3$ was also found to be incorporated in the hydrates in the form of monocarboaluminates (Kelham, 1998).

An investigation of the total $Ca(OH)_2$ in the outer 10mm cover zone revealed that the increased degree of hydration was accompanied by a slight increase in the total $Ca(OH)_2$, and this was the case in all mixes with increasing limestone filler content. The combination of the concrete physical and chemical properties had influence over the carbonation resistance of the limestone filled CEM II concrete.

Table 6.10 Hydration study of Test Series 4 mixes.

Mix and % Limestone Filler Replacement		Degree of Hydration [1], %		Total $Ca(OH)_2$, % wt of cover zone concrete[1]	
		Pre-entry	2 Years	Pre-entry	2 Years
PC/PFA30%	0%	59	79	1.7	0.7
	5%	59	70	1.7	0.7
	10%	60	71	1.8	0.7
	15%	58	72	1.7	0.8
	20%	59	73	1.7	0.9
PC	0%	69	74	5.2	4.3
	5%	69	74	5.2	4.3
	10%	68	75	5.2	4.4
	15%	69	75	5.2	4.4
	20%	70	76	5.3	4.5
MK 10%	0%	55	68	4.3	1.2
	5%	56	69	4.4	1.2
	10%	55	70	4.4	1.3
	15%	54	70	4.3	1.3
	20%	55	71	4.4	1.4
MK 15%	0%	49	64	1.6	0.6
	5%	47	64	1.6	0.6
	10%	49	65	1.5	0.6
	15%	41	66	1.5	0.7
	20%	42	67	1.6	0.8
MK 20%	0%	48	63	1.3	0.6
	5%	47	64	1.2	0.6
	10%	48	65	1.3	0.6
	15%	48	67	1.3	0.7
	20%	48	67	1.3	0.7
CSF 10%	0%	54	66	1.5	0.5
	5%	55	66	1.5	0.5
	10%	56	67	1.6	0.6
	15%	56	68	1.6	0.7
	20%	55	69	1.6	0.8
CSF 15%	0%	51	64	1.4	0.5
	5%	50	65	1.4	0.5
	10%	51	65	1.4	0.6
	15%	51	66	1.4	0.7
	20%	51	66	1.4	0.7
CSF 20%	0%	54	66	1.3	0.5
	5%	53	67	1.2	0.5
	10%	54	67	1.3	0.6
	15%	55	68	1.4	0.6
	20%	55	69	1.4	0.6

[1] Measured to a depth of 10mm

However, above the optimum level of fines, the physical properties were more significant at higher replacement levels as carbonation depths increased, despite the cover zone $Ca(OH)_2$ being slightly greater after 2 years CEN carbonation.

6.6 SUMMARY

The influence of coarse aggregate type and fines content were examined to ascertain their effects on the carbonation resistance of concrete. The inclusion of various coarse aggregate types, both crushed rock and natural gravel commonly used within the UK appeared to make little difference to the carbonation performance of the concrete. Closer inspection of the physical and chemical mix properties revealed that mixes containing crushed rock aggregates had a lower cement content and higher water/PC ratio than the Reference Mix, and the reduced permeation properties in the cover zone offset the potential poorer chemical carbonation resistance from these mixes. This phenomenon highlighted the caution that must be observed in specifying different coarse aggregate types, and an appraisal of the potential changes in mix proportions must be carried out to determine the potential influence on chemical and physical characteristics of the hardened concrete.

The influence of fine aggregate and fine particles was also examined to determine the effects of increasing the fines content of the mix to improve the packing density and void ratio of CEM II concrete. The fine/coarse aggregate ratio was adjusted in an attempt to increase the overall fines content with the result that both permeation properties and carbonation resistance were detrimentally affected. The particulate packing, and subsequent voids within the hardened concrete, prior to exposure to carbonation, were investigated by means of an integrated Dewar-Powers-Brownyard model which considered the packing of the mix constituents and subsequent effects of hydration. The adjusted fine/coarse aggregate ratio mixes showed a reduction in packing density, indicating that merely increasing the fine/coarse aggregate ratio did not substantially affect the fines (<125μm) content of the concrete. It did, however, produce an excess of particles in the size range 300-600μm leading to particle interference and wall effects between the mortar and coarse aggregates.

An investigation of the mortar component of CEM I and CEM II concretes showed that in order to reduce the void ratio to the optimum, the paste component had to be increased. Partial replacement of the fine aggregate with a fine limestone filler was proposed and, from the theoretical calculations, the packing densities and void ratios were improved.

The subsequent permeation properties and carbonation resistance of the CEM II concretes were improved and an optimum fines content of 395 ± 5kg/m^3 proposed to ensure that the carbonation performance of the CEM II concrete was similar or better to that of the PC/ PFA30% Reference Mix. The limestone filler in the concrete did not affect the chemical characteristics of the cover zone within the first few days (up to $0.5f_{cm,28}$) , although at 2 years, limestone filled mixes showed an increased degree of hydration compared to those without filler. The long term chemical benefits of limestone filler were outweighed by the physical effects, as was observed in mixes with >10% limestone replacement where carbonation depths were greater due to the reduction in packing density.

CHAPTER 7

ESTIMATING LONG TERM CARBONATION PERFORMANCE

7.1 INTRODUCTION

The final phase of the study focussed on estimating the long term carbonation performance of CEM II concrete using the data obtained from the enhanced CEN Test. The work carried out within the current study had identified the importance of the near surface characteristics and the degree of pore saturation on the carbonation resistance of hardened concrete. The use of a single parameter to identify potential carbonation performance, such as permeation, has been commonly employed by a number of researchers (Parrot, 1987), however the current study of CEM II concrete intimated that caution must be taken when specifying concrete on the basis of a single characteristic, be it physical or chemical. CEM II concretes with higher levels of CSF and MK, had excellent near surface permeation properties, however the cover zone chemistry was such that the alkalinity was reduced compared to PC mixes. This was due to a combination of the mix proportions and pozzolanic reactions associated with the materials.

The long term carbonation performance, up to 35 years, was estimated from a combination of the physical and chemical characteristics of the hardened concrete prior to exposure to the carbonating environment. The minimum intended working life of 50 years, given in BS 8500, includes the time for the concrete to carbonate (initiation period) and time for steel to corrode (propagation period). As stated in Chapter 2, a conservative approach was adopted by Hobbs (1998), in which the initiation period was 35 years and the propagation period taken as 15 years. This conservative approach was adopted in the analysis of published carbonation data and estimation of long term performance of CEM II concrete.

The enhanced CEN test consisted of three Exposure Classes in an attempt to approximately replicate natural conditions traditionally found in structures subjected to carbonation. A comprehensive climatological study of atmospheric conditions within the UK and throughout Europe was carried out to determine similarities between the CEN test Exposure Classes and the natural environment. A long term exposure site was established and 1 year carbonation data compared to that of the enhanced CEN test.

7.2 ESTIMATING LONG TERM CARBONATION

A number of empirical and theoretical models are based on the fundamental relationship between depth of carbonation and time:

$$d_c = k\, t^n \qquad (7.1)$$

where d_c is the depth of carbonation, k is a constant relating to the rate of carbonation, t is time and n is an empirical constant.

The mixes tested in Series 1 were analysed up to period of 2 years by 2 methods to determine the validity of the $d=kt^n$ relationship for CEM II concrete.

7.2.1 Curvilinear Regression of CEN Carbonation Data up to 2 Years

In the first instance, the CEN carbonation data was analysed up to period of 2 years across all Exposure Classes to determine whether the parameters defining the regression curve were constant or otherwise over the test period. As stated in Chapter 5, an ANOVA test had determined that the relative ranking of cement types in the test was constant after a period of 18 months in Exposure Class 1, 1 year in Exposure Class 2 and at all times during the test in Exposure Class 3.

The data up to a period of 2 years was non-linearly regressed using the least squares method (Kennedy and Neville, 1976) and fitted to a power regression formula in the form:

$$y = c\, x^b \qquad (7.2)$$

The constants, c and b, or in the case of the current study, k and n, were analysed at 1 year, 18 months, and 2 years to observe the variation across the test period.

The constants calculated for each cement type up to a period of 2 years are given in Table 7.1. In Exposure Class 1, the mean 'n' value was found to be 0.49 after 1 year with a coefficient of variation of 9.5%. Up to a period of 2 years the variability reduced to 3.1%, while the mean 'n' value was the same at 1.5 years and 2 years. The mean calculated 'k' value was also similar at 1.5 and 2 years, indicating some degree of stability in the CEN test, as had been confirmed in Chapter 5.

Table 7.1 Power fit regression values for Test Series 1 mixes up to a period of 2 years.

Mix	Values Calculated at 1 year		Values Calculated at 1.5 years		Values Calculated at 2 years	
	n	k	n	k	n	k
Class 1 Exposure						
PC/PFA 30%	0.55	4.15	0.51	3.97	0.51	3.94
PC	0.57	2.18	0.50	2.11	0.50	2.10
MK 10%	0.45	1.73	0.48	1.71	0.48	1.82
MK 15%	0.45	5.90	0.49	5.78	0.48	5.76
MK 20%	0.49	5.71	0.48	5.43	0.48	5.34
CSF 10%	0.48	5.61	0.47	5.44	0.47	5.32
CSF 15%	0.46	5.13	0.46	5.72	0.47	5.91
CSF 20%	0.46	5.35	0.47	6.02	0.47	6.02
Mean	*0.49*	*4.47*	*0.48*	*4.52*	*0.48*	*4.53*
σ	*0.05*	*1.65*	*0.02*	*1.73*	*0.01*	*1.71*
V, %	*9.5*	*36.8*	*3.5*	*38.3*	*3.1*	*37.8*
Class 2 Exposure						
PC/PFA 30%	0.49	2.71	0.51	2.59	0.48	2.53
PC	0.49	1.44	0.52	1.51	0.48	1.56
MK 10%	0.42	1.05	0.39	1.12	0.40	1.21
MK 15%	0.43	5.27	0.44	5.03	0.41	4.88
MK 20%	0.43	4.43	0.42	4.16	0.40	3.88
CSF 10%	0.41	3.09	0.39	2.91	0.40	2.86
CSF 15%	0.40	3.75	0.41	3.66	0.41	3.65
CSF 20%	0.39	3.80	0.41	3.70	0.40	3.68
Mean	*0.43*	*3.19*	*0.44*	*3.09*	*0.42*	*3.03*
σ	*0.04*	*1.44*	*0.05*	*1.32*	*0.04*	*1.24*
V, %	*8.8*	*45.0*	*11.7*	*42.9*	*8.5*	*40.8*
Class 3 Exposure						
PC/PFA 30%	0.41	1.74	0.41	1.74	0.41	1.74
PC	0.40	1.25	0.40	1.25	0.40	1.25
MK 10%	0.37	1.20	0.37	1.20	0.37	1.20
MK 15%	0.37	2.37	0.37	2.37	0.37	2.37
MK 20%	0.37	2.79	0.37	2.79	0.37	2.79
CSF 10%	0.37	2.53	0.37	2.53	0.37	2.53
CSF 15%	0.37	2.82	0.37	2.82	0.37	2.82
CSF 20%	0.37	2.99	0.37	2.99	0.37	2.99
Mean	*0.38*	*2.21*	*0.38*	*2.21*	*0.38*	*2.21*
σ	*0.02*	*0.72*	*0.02*	*0.72*	*0.02*	*0.72*
V, %	*4.3*	*32.5*	*4.3*	*32.5*	*4.3*	*32.5*

A similar phenomenon was also observed in Exposure Class 2 and Exposure Class 3, with 'n' and 'k' values being constant in Exposure Class 3 at 1 year and 2 years. Figure 7.1 compares the predicted depths of carbonation at 35 years from the power fit regression curves across all cement types in Test Series 2, and compares this to the minimum cover specified in BS 8500 for Exposure Classes XC1 and XC3/4. The Figure compares the estimated 35 year carbonation depths with 'n' and 'k' values calculated at 1, 1.5 and 2 years. The importance of both the 'n' and 'k' value are evident, especially in Exposure Class 1. For example, in the PC/PFA 30% Reference Mix, a reduction in 'n' from 0.55 to 0.51, and corresponding reduction in 'k' of 4.15 to 3.97, reduced the estimated carbonation depth from 29mm to 25mm. Abbas (2000) determined that the 'k' value was the most influential of the constants with regards to the estimated carbonation depth (Abbas, 2000). The 'k' value represents the potential carbonation rate of concrete which will be influenced by a number of factors, especially the physical and chemical characteristics of the concrete (Parrott, 1990a).

7.2.2 Development of Multi Regressive Estimation Model

The development of a multi regressive estimation model for carbonation involved the consideration of finding a simplified, but best possible solution to the complex relationship between a number of explanatory variables and a response variable. The 'k' factor in the curvilinear regression was assumed to the be the most influential variable affecting the ingress of carbonation, and was analysed first. In the development of the model, two explanatory variables were considered:

i) The cover zone permeation properties;
ii) The near surface $Ca(OH)_2$ content of the cover concrete.

The response variable was the depth of carbonation at two years. The two year depth of carbonation was chosen as it was felt that measurement at this test age was more reliable than at 1 year, where depths of carbonation were relatively small and there was a greater margin for experimental error.

The principle of the development of the model is that the relationship between the explanatory variables and response variable is fitted to the data by the least squares method, and the model validated by hypothesis testing of the parameters governing the model, in this case the permeation and cover zone chemistry.

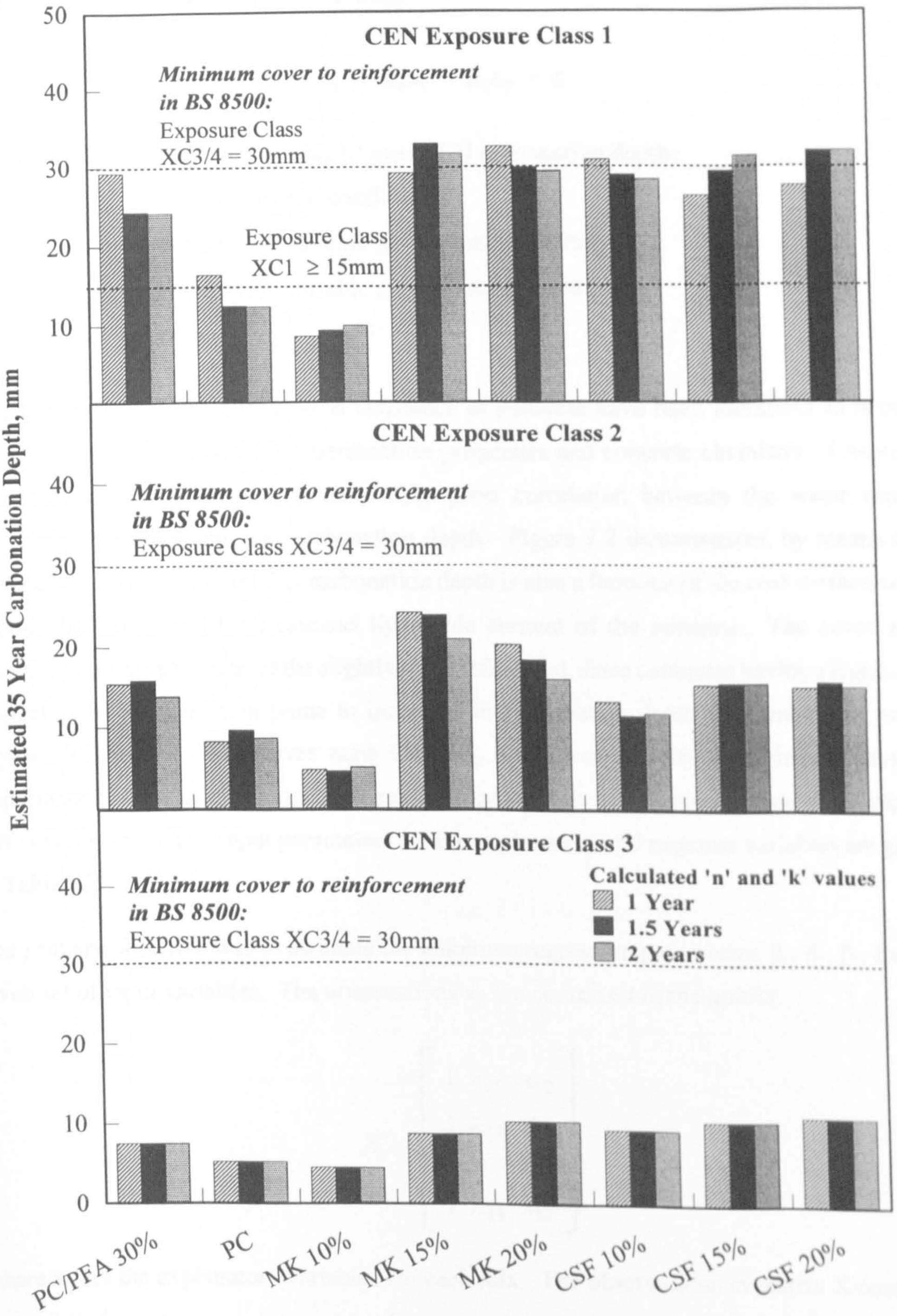


Figure 7.1 Estimated 35 year carbonation depths for Test Series 1 mixes in CEN Exposure Classes 1, 2 and 3.

The multi-regression model takes the form:

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \varepsilon \qquad (7.3)$$

where: Y = response variable (2 year CEN carbonation depth)

β_0, β_1, β_2, = regression coefficients

x_1 = explanatory variable (cover zone chemistry)

x_2 = explanatory variable (cover zone permeation)

ε = error

The factors influencing carbonation resistance of concrete have been identified as being a combination of the near surface permeation properties and concrete chemistry. Chapter 6 demonstrated that there was a reasonably good correlation between the water vapour diffusivity, fines content, and carbonation depth. Figure 7.2 demonstrates, by means of a surface plot, that the 2 year CEN carbonation depth is also a function of the near surface water vapour diffusivity and total calcium hydroxide content of the concrete. The cover zone $Ca(OH)_2$ content appears to be the slightly more influential, since concretes having a high cover $Ca(OH)_2$ content were less prone to increases in carbonation depth with increasing water vapour diffusivity. The cover zone $Ca(OH)_2$ was given priority, in terms of physical importance to the model, and labelled explanatory variable x_1. The cover zone water vapour diffusivity was x_2. The input parameters for the explanatory and response variables are given in Table 7.2.

The primary objective was to estimate the unknown regression parameters, β_0, β_1, β_2, for the given set of input variables. The observations x_{ij} are contained in the matrix:

$$X = \begin{bmatrix} 1 & x_{11} & x_{12} \\ 1 & x_{21} & x_{22} \\ \vdots & \vdots & \vdots \\ 1 & x_{81} & x_{82} \end{bmatrix} \qquad (7.4)$$

where x_{ij} are the explanatory variables for each mix. The observations in matrix X contain a row of 1's in order to accommodate the numerical constant β_0 in the model. The multi-regression model is written as:

$$Y = X\beta + \varepsilon \qquad (7.5)$$

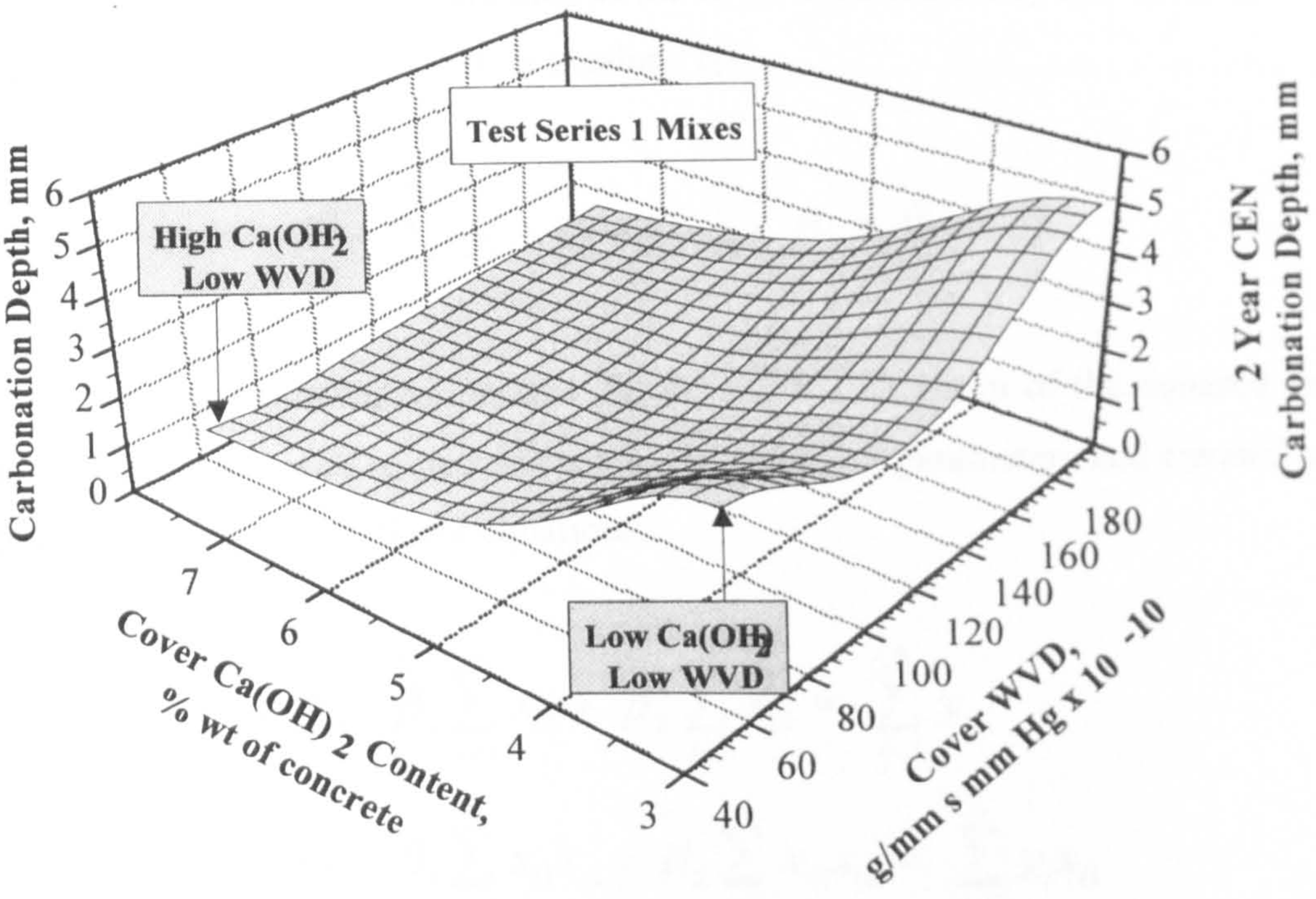


Figure 7.2 Relationship between pre-entry chemical and physical properties and 2 year CEN carbonation depth.

Table 7.2 Input parameters for stage 1 of estimation model.

Mix	Explanatory Variables		Response Variable
	x_1	x_2	Y
1	1.7	112	5.5
2	5.4	192	3.0
3	4.3	51	3.0
4	1.6	70	7.0
5	1.3	77	7.5
6	1.5	58	6.5
7	1.4	64	7.0
8	1.3	68	7.5

The least square solution to the regression of the cover zone chemistry and cover zone WVD to the 2 year CEN carbonation depth is obtained by:

$$S^2 = \sum_{i=1}^{n} (y_i - \beta_0 - \beta_1 x_1 - \beta_2 x_2)^2 \tag{7.6}$$

with respect to the unknown parameters β_0, β_1, and β_2. The sum of the squared errors is partially differentiated with respect to each of the unknown parameters and equated to zero, giving the following normal linear equations:

$$n \hat{\beta}_0 + \hat{\beta}_1 \sum_{i=1}^{n} x_{i1} + \hat{\beta}_2 \sum_{i=1}^{n} x_{i2} = \sum_{i=1}^{n} y_i \tag{7.7}$$

$$\hat{\beta}_0 \sum_{i=1} x_{i1} + \hat{\beta}_1 \sum_{i=1}^{n} x_{i1} x_{i1} + \hat{\beta}_2 \sum_{i=1}^{n} x_{i1} x_{i2} = \sum_{i=1}^{n} y_i x_{i1} \tag{7.8}$$

which gives the estimators ($\hat{\beta}$) for the parameters in the model.

Equations 7.7 and 7.8 may be represented in the matrix form by:

$$\hat{\beta} = (\mathbf{X}^T\mathbf{X})^{-1} \mathbf{X}^T\mathbf{y} \tag{7.9}$$

where T is the transpose of the observations matrix x_{ij}.

For the current set of input parameters, the model fitted to the cover zone $Ca(OH)_2$ and WVD is:

$$8.38 - 1.21x_1 + 0.003x_2 = Y \tag{7.10}$$

The degree of error within the model is established by calculating the error variance, shown in Table 7.3. In this case, at a 95% confidence level, the carbonation estimated error variance, σ^2, is within the band 0.025 and 0.995mm. The significance of the relationship between the explanatory variables and response variable is tested by an analysis of variance (ANOVA) test Table 7.4. The null hypothesis, H_0:$\beta_i = 0$, that is, the response variable is not influenced by the explanatory variables, is tested for significance. In this case, the hypothesis is rejected indicating that both cover $Ca(OH)_2$ content and WVD influence the carbonation depth.

Table 7.3 Establishing the degree of error within the multi-regressive carbonation model.

Establish unbiased estimator of σ^2	$\hat{\sigma} = \frac{y^T y - \hat{\beta} X^T y}{n-p}$	$\hat{\sigma} = 0.4116$
Establish 95% confidence limits on error variance	$\frac{(n-p)\hat{\sigma}^2}{\sigma^2}$ has a χ^2 distribution	From statistical tables (Kennedy and Neville, 1976) $\chi^2_{5,0.975} = 16.7$ $\chi^2_{5,0.025} = 0.412$
Error variance σ^2	$0.025 < \sigma^2 < 0.955$	

Table 7.4 ANOVA results to establish significance of model parameters, β_0, β_1, β_2

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F Value
Regression	2	22.817	11.409	27.717
Residual	5	2.058	0.412	
Total	*7*	*24.875*		

Null hypothesis: H_0: $B_i = 0$. From statistical tables, $F_{2,5,0.05} < F$ therefore the null hypothesis is rejected at a 95% confidence level and we can confidently say that carbonation depth is related to both cover zone $Ca(OH)_2$ content and cover zone WVD

A similar analysis was carried out for the limestone filled CEM II concretes in Test Series 4, and the influence of the limestone filler reduction was accounted for by means of a permeation factor whereby:

$$Y = X\beta(\frac{10}{P}) + \varepsilon \qquad (7.11)$$

Where (10/P) is the permeation factor, and P is the cover zone water vapour diffusivity.

Figures 7.3 and 7.4 compare the 2 year CEN carbonation depths predicted from the multi regressive model and the actual carbonation depths, measured at 2 years for the non-limestone filled and limestone filled concretes respectively. A reasonably good correlation was found between the estimated and measured depths of carbonation, all of which were within the estimated 95% confidence limits of the model.

The near surface qualities of the concrete have been taken into account by consideration of the cover zone $Ca(OH)_2$ content and the cover zone water vapour diffusivity. In order to estimate the longer term carbonation depth of concrete, a time factor and consideration of the surrounding environment must be introduced. The multi regressive model developed between the cover zone concrete characteristics and carbonation depth accounts for the factor 'k' in the relationship given in Equation 7.1. The factor 'n' in the relationship will primarily be a function of the environment in which the concrete will service (Parrott, 1994b). In structures exposed to a nautral carbonation environment, three degrees of mositure availability are assumed (other than the structure being completely submerged in water):

i) *Indoor Exposure* - low relative humidity;

ii) *Outdoor Sheltered Exposure* - elements exposed to the atmosphere but sheltered from the effects of direct precipitation;

iii) *Outdoor Unsheltered Exposure* - elements exposed to the atmosphere including the direct effects of precipitation.

From the current enhanced CEN test, three exposure classes were tested in an attempt to ascertain whether the three conditions experienced in the natural environment could be replicated simply in the laboratory.

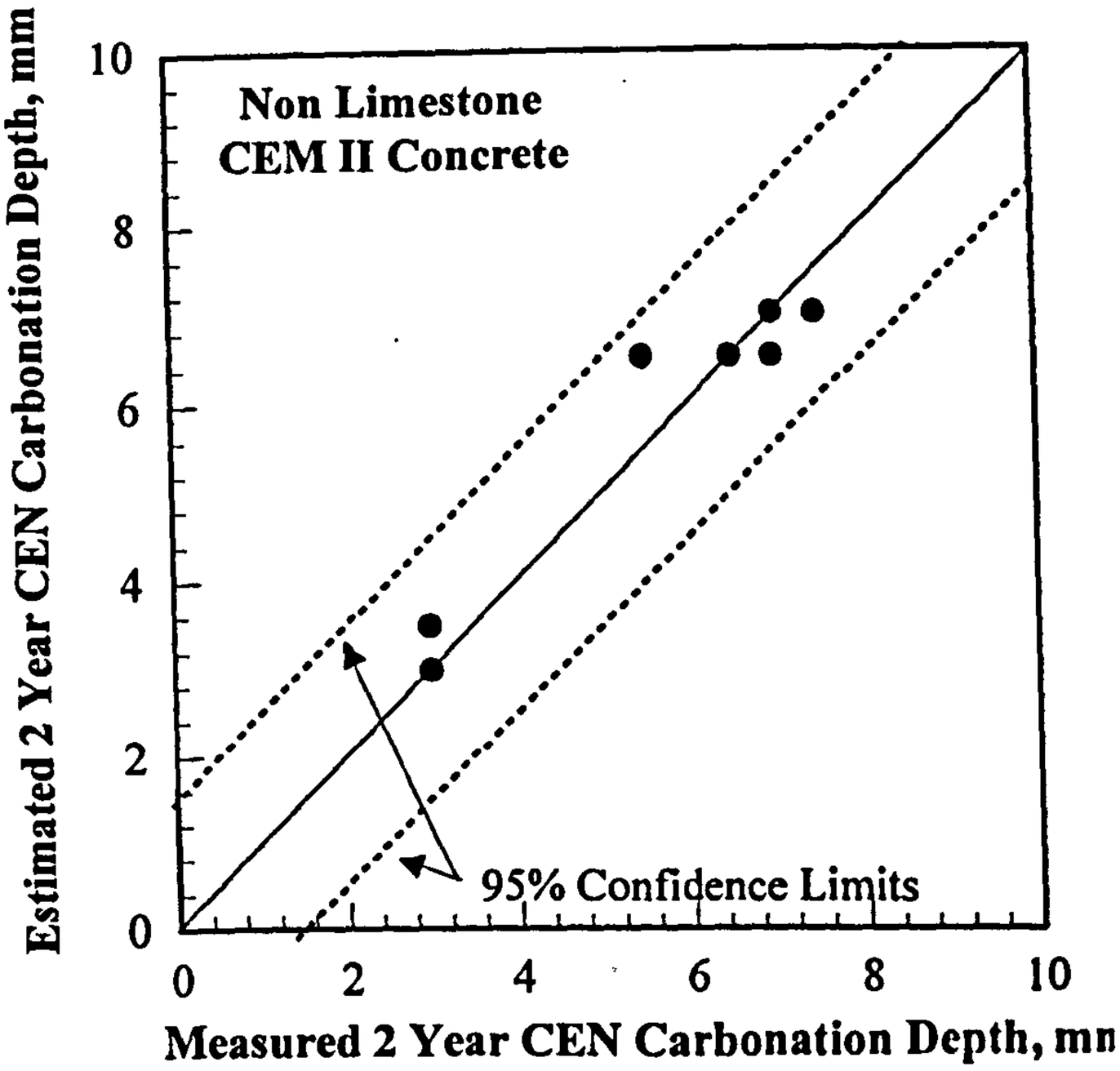


Figure 7.3 Comparison of measured and estimated 2 year CEN carbonation depths for Stage 1 of estimation model for non limestone filled CEM II concrete.

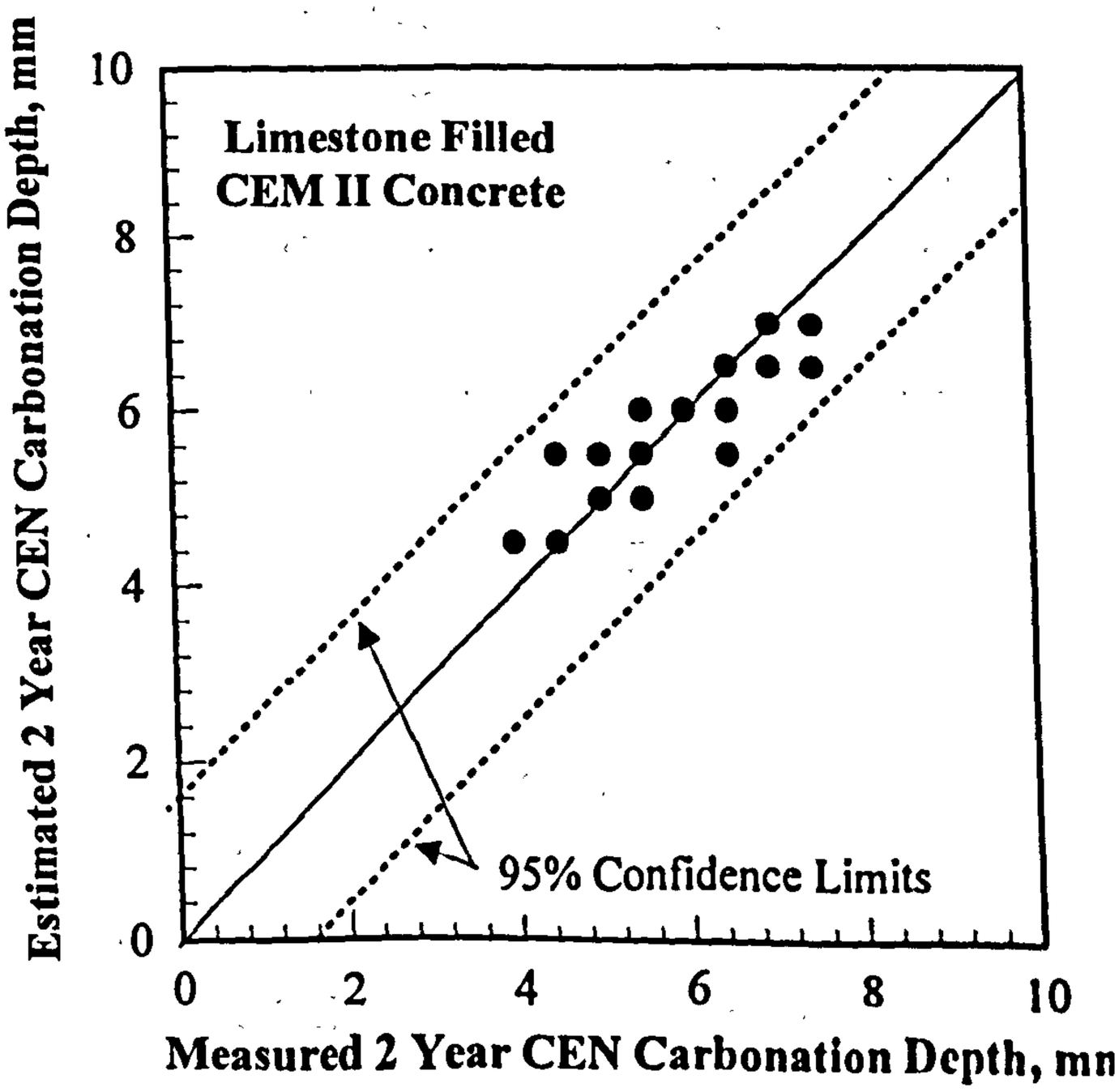


Figure 7.4 Comparison of measured and estimated 2 year CEN carbonation depths for Stage 1 of estimation model for limestone filled CEM II concrete.

Determination of the influence of moisture was deemed to be through the variation in the 'n' factor as the 'k' factor was primarily dependent on the concrete properties. The non linear regression analysis carried out using the least squares method, and the power-fit equation $y=cx^b$, gave a reasonable spread of 'n' values across the cement types. Table 7.1 details the 'k' and 'n' values for Test Series 1 concretes and shows that, across all cement types, after two years, the average 'n' value was 0.48 for Exposure Class 1, 0.42 for Exposure Class 2 and 0.38 for Exposure Class 3. The 'n' values directly reflected the influence of the environment, and the values were similar to those found by a Parrott (1994b) in his survey of structures in the field.

Within each cement type there was a degree of commonality amongst the 'n' values indicating that each cement type has a different sensitivity to exposure to moisture. The PC/PFA 30% Reference Mix and PC mix had similar 'n' values within each Exposure Class, and this value reduced with increasing exposure to moisture.

The remaining MK and CSF mixes also acted in a similar manner up to a period of two years, with 'n' values reducing with increasing exposure to moisture. It is interesting to note that in Exposure Class 3, the 'n' values did not vary with time in any concrete, reflecting the findings of the analysis of variance to determine 'test stability' earlier on in the current study. For the purposes of the current estimation model, the 'n' values obtained from the non-linear regression analysis of the 2 year data were adopted as shown in Table 7.5

The multi regressive model for estimating carbonation depth of hardened concrete takes the general form:

$$d_c = (\beta_0 + \beta_1 C + \beta_2 P)\, t^n \qquad (7.12)$$

where d_c = depth of carbonation, mm after time t

$\beta_0, \beta_1, \beta_2,$ = empirical constants

C = total $Ca(OH)_2$ content within 10mm cover zone of concrete

P = water vapour diffusivity of concrete cover zone

Figure 7.5 compares the actual measured data up to 2 years in the CEN test with that of the model for the PC/PFA 30% Reference mix, the PC mix and a CSF 10% in selected Exposure Classes, indicating that the model developed fits the data reasonably well up to 2 years.

Table 7.5 Values of 'n' adopted for the multi-regressive model, obtained from the non-linear regression analysis of CEN 2 year carbonation depths.

Mix	Exposure Class 1	Exposure Class 2	Exposure Class 3
PC/PFA 30%, PC	0.50	0.48	0.40
MK 10%, 15%, 20%	0.50	0.40	0.30
CSF 10%, 15%, 20%	0.50	0.40	0.30

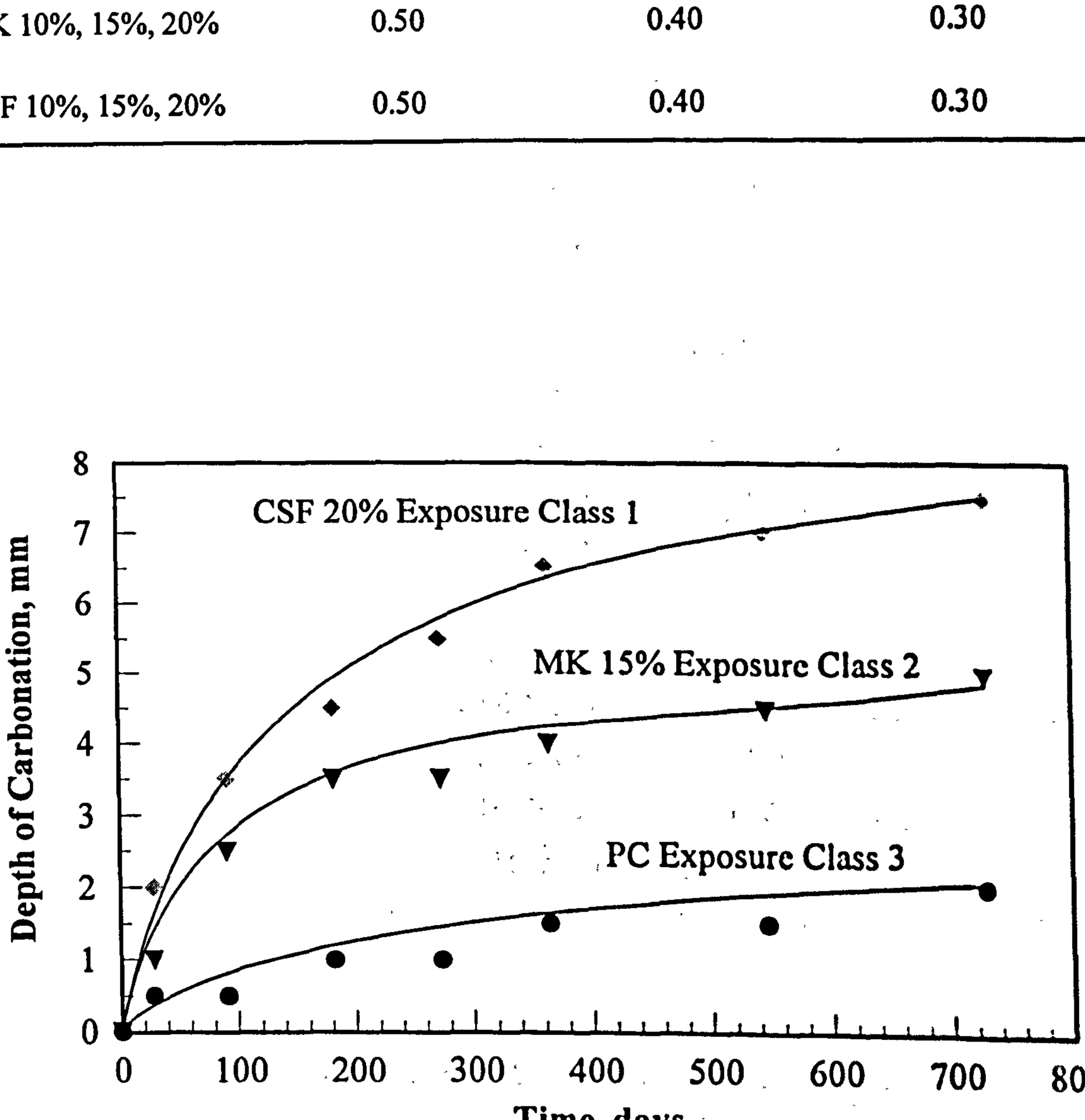


Figure 7.5 Comparison of measured carbonation depths with multi-regressive model developed for various concrete types in CEN Exposure Classes 1, 2 and 3. The data points are the measured carbonation depths.

The theory behind the development of the multi-regressive estimation model is that the long term performance of concrete in a carbonating environment can be estimated from a knowledge of:

i) The cover zone chemistry;
ii) The cover zone permeation properties;
iii)The environment in which the concrete will exist

The development of a multi regressive model, taking into account only these three fundamental parameters, has the potential to allow the engineer to select a cement or concrete type on the basis of simple concrete characteristic measurements rather than dealing with unnecessarily complicated equations. From the work carried out in Chapter 5, it was noted that the water/PC ratio reflected the carbonation resistance and, to all intents and purposes, the water/PC ratio heavily influences the initial total calcium hydroxide content of the cover zone. Figure 7.6 illustrates the relationship between the estimated 35 year carbonation, depth using the multi-regressive estimation model and the water/PC ratio of the mixes. A similar relationship was determined at 35 years compared to 2 years with a limiting factor of approximately 0.65 water/PC ratio being observed in Exposure Class 1.

The Figure also compares the estimated depths of carbonation to the minimum cover requirements given in the standard BS8500-1:2001. Although BS 8500 states a minimum cover of 30mm for a grade C35 concrete, the comparison made here for the purpose of the study is made on a 37N/mm^2 concrete. In Exposure Class 1, the majority of concretes in CEM II are estimated to carbonate beyond 15mm after 35 years exposure however, given that a degree of moisture is required for steel corrosion to occur, it is unlikely that this will be a problem in this environment.

Exposure Class 2 estimates a maximum carbonation depth of approximately 20mm after 35 years which is 10mm below the minimum cover required in BS 8500-1:2001. All mixes in Exposure Class 3 are also deemed to have a satisfactory performance. From the initial analysis of the extent of wetting of specimens in Exposure Class 3, it is unlikely that is fully representative of outdoors exposure, since the specimens are very rarely dry. In typical structural conditions, carbonation induced corrosion would be very unlikely, as the rate of carbonation would be hindered by the degree of pore fluid saturation.

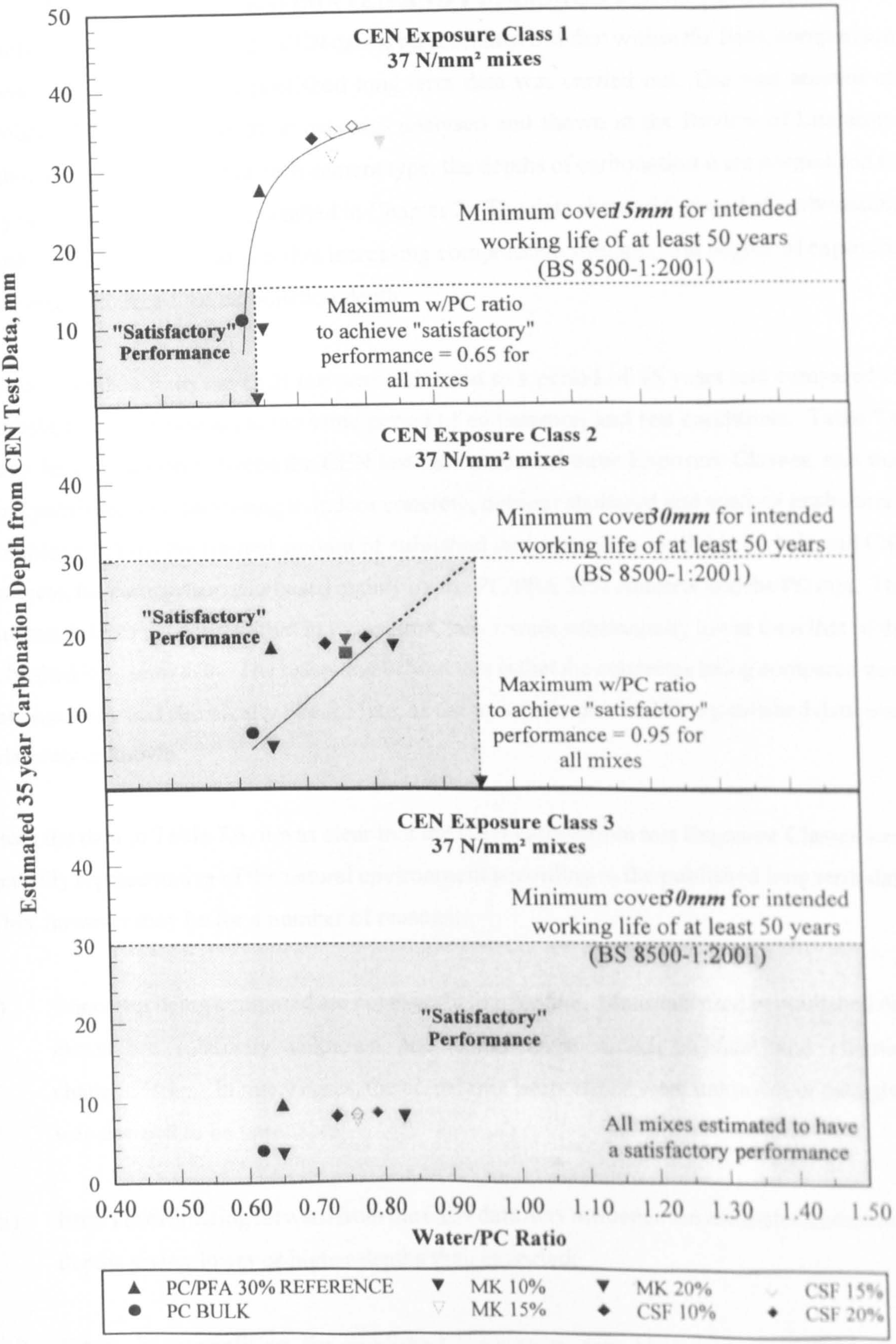


Figure 7.6 Estimated long term relationship between carbonation depth and water/PC ratio of Test Series 1 concrete.

7.3 COMPARISON OF ESTIMATED AND PUBLISHED LONG TERM DATA

In order to establish whether the CEN data is representative of that within the field, comparison between the CEN data and published long term data was carried out. The vast amount of published long term carbonation data was analysed and shown in the Review of Literature within the current study. For each cement type, the depths of carbonation were normalised to 35 years using the procedure detailed in Chapter 2. The data showed a spread of carbonation depths, however, the trend was that increasing compressive strength, and degree of exposure to moisture, reduced the carbonation depth.

The current data from the CEN test was estimated to a period of 35 years and compared to published data normalised to the same period of carbonation and test conditions. Table 7.6 gives the comparison between the CEN test data across all three Exposure Classes, and that from published data pertaining to indoor concrete, outdoor sheltered and outdoor unsheltered conditions. Given the limited amount of published long term data available on MK and CSF concrete, the comparison was based mainly on the PC/PFA 30% concrete and the PC mix. The estimated depths of carbonation in Exposure Class 1 were substantially lower than that of the published long term data. The reasoning behind this is that the concretes being compared were not physically and chemically like for like, as the exact mix details of the published data were relatively unknown.

From the data in Table 7.6, it was clear that the CEN carbonation test Exposure Classes were not fully representative of the natural environment according to the published long term data. This, however may be for a number of reasons:

i) Concretes being compared are not exactly like for like. Materials used in published data mixes are relatively unknown and could have varied physical and chemical characteristics. In many cases, the actual mix proportions were unknown or data given was deemed to be unreliable;

ii) Errors in estimating forward from the CEN data may influence the estimated carbonation depths giving lower or higher depths than expected;

iii) Errors in normalising the published long term data to a test age of 35 years. Interpolation or extrapolation of the carbonation depths from the published data could lead to erroneous results.

Table 7.6 Comparison of predicted 35 year carbonation depths from current study with available published long term carbonation data. All mixes are compared on an equal strength basis of 37N/mm^2.

Mix	Estimated 35 Year Carbonation Depth from Current Study, mm			35 Year Carbonation Depth from Published Long Term Data		
	Exposure Class 1	Exposure Class 2	Exposure Class 3	Indoor Concrete	Outdoor Sheltered	Outdoors Unsheltered
PC/PFA30%	27.5	18.5	10.0	55.0	25.0	12.0
PC	11.5	7.5	4.0	46.0	24.0	11.0
MK 10%	10.0	5.5	3.5	l.d.	32.0	12.0
MK 15%	31.5	17.5	7.5	l.d.	l.d.	l.d.
MK 20%	33.5	18.5	8.0	l.d.	l.d.	l.d.
CSF 10%	34.0	19.0	8.5	l.d.	30.0[1]	l.d.
CSF 15%	34.5	19.5	8.5	l.d.	l.d.	l.d.
CSF 20%	35.0	20.0	8.5	l.d.	l.d.	l.d.

[1] Data is for 5% CSF, 35N/mm^2 concrete.

l.d. Limited published data available.

From the comparison of the estimated long term carbonation performance with the published long term data, it was evident that the conditions which were most likely to encourage carbonation induced corrosion, outdoors sheltered or outdoors unsheltered, were difficult to predict purely by means of wetting and drying cycles in the CEN test. Across the cement types studied, outdoors sheltered conditions appeared to lie somewhere between Exposure Class 1 and Exposure Class 2. Hence, the degree of wetting was too frequent in Exposure Class 2.

7.3.1 Long Term Carbonation of Limestone Filled Concrete

The inclusion of limestone filler was found to enhance the carbonation resistance of concrete up to a fine aggregate replacement level of approximately 10%. This was attributed to the improved packing density associated with the replacement of a coarser material with a fine particulate component and the refinement of the cover zone pore structure which was determined through improved permeation properties.

Table 7.7 compares the estimated 35 year carbonation depths of the CEM I and CEM II concretes with and without the replacement of a volume fraction of the fine aggregate with limestone filler. As with the 2 year carbonation data, the optimum limestone filler replacement level is approximately 10% by weight of the fine aggregate. The shaded values in Table 7.7 are those which are within the minimum cover depth of 30mm specified in BS 8500-1 for a minimum intended working life of at least 50 years. The optimum levels of limestone filler substantially reduce the 35 year estimated carbonation depths and all concrete containing CEM II cements show a satisfactory performance, that is the depth of carbonation is less than 30mm at 35 years. These values are shown in bold.

This substantial enhancement of carbonation resistance afforded by the replacement of fine aggregate with limestone filler has the potential to provide a trade-off between concrete cover qualities to obtain the intended working life as stated in BS 8500-1. Using the sensitivity analysis from Chapter 5, the limestone filled mixes were analysed and potential trade-off evaluated. Table 7.8 shows the potential trade-off between the concrete grade, cover depth and level of limestone filler replacement in order to achieve an estimated carbonation depth of 30mm after 35 years. The data is compared to carbonation depths estimated from Exposure Class 1. The analysis shows that the partial volumetric replacement of fine aggregate with limestone filler allows a reduction in concrete grade or a reduction in cover depth to achieve a specified minimum intended working life.

Table 7.7 Estimated 35 year carbonation depths of concrete containing limestone filler.

Mix	Estimated 35 Year Carbonation Depth, mm				
	0%[1]	**5%[1]**	**10%[1]**	**15%[1]**	**20%[1]**
PC/PFA30%	27.5	**22.0**	23.5	26.0	27.5
PC	11.5	9.0	**8.0**	9.0	10.0
MK 10%	10.0	6.0	**6.0**	10.0	11.0
MK 15%	31.5	26.5	**23.0**	26.5	29.5
MK 20%	33.5	28.5	**22.5**	26.5	31.0
CSF 10%	34.0	28.0	**24.0**	27.0	34.0
CSF 15%	34.5	29.5	**25.5**	29.5	31.0
CSF 20%	35.0	28.5	**26.5**	28.5	31.0

[1] Percentage limestone filler / fine aggregate replacement
Shaded values less than 30mm, bold values are minimum carbonation depths

Table 7.8 Potential trade off between limestone filler replacement, concrete grade and cover depth to achieve a minimum intended working life of 50 years in BS 8500-1.

Mix	Minimum Concrete Grade [2], N/mm²				Minimum Cover Depth [3] at 37N/mm², mm			
	0%[1]	5%[1]	10%[1]	15%[1]	0%[1]	5%[1]	10%[1]	15%[1]
PC/PFA30%	34.0	32.0	33.0	34.0	30.0	25.0	25.0	25.0
PC	30.0	29.0	27.0	29.0	25.0	20.0	20.0	25.0
MK 10%	29.0	27.0	27.0	29.0	25.0	20.0	20.0	25.0
MK 15%	38.0	37.0	35.0	37.0	35.0	30.0	25.0	30.0
MK 20%	39.0	37.0	35.0	36.0	35.0	30.0	25.0	30.0
CSF 10%	40.0	37.0	35.0	36.0	35.0	30.0	25.0	30.0
CSF 15%	40.0	38.0	35.0	37.0	35.0	35.0	25.0	30.0
CSF 20%	41.0	38.0	35.0	38.0	35.0	35.0	25.0	30.0

[1] Percentage limestone filler / fine aggregate replacement
[2] Minimum grade in BS 8500 for Exposure Class XC3/4 is ***35N/mm²***.
[3] Minimum cover depth for Exposure Class XC3/4, grade 35N/mm² concrete is ***30mm.***
Shaded values are zones of potential trade off.

In the case of CEM II concretes containing higher replacement levels of MK and CSF, the minimum grade and cover depth specified may not be sufficient to provide a minimum intended working life of 50 years. For example, at 37N/mm^2, the MK 20% concrete was estimated to have a 35 year carbonation depth of 33.5mm. The desired wokring life could potentially be achieved by either increasing the cover depth to 35mm or increasing the concrete grade to 39N/mm^2. The optimum level of fine aggregate/limestone filler replacement was approximately 10% by weight although replacement levels of 5% and 15% still improved the carbonation resistance of CEM II concretes by improving the packing density and near surface permeation properties.

7.4 CLIMATOLOGICAL STUDY OF UK AND EUROPE

The variability between the CEN test results and published carbonation data was attributed to a number of factors, one of which was the environmental conditions to which the concrete is exposed. The degree of exposure to moisture has a major influence on the carbonation rate of concrete (Parrott, 1987). The internal pore environment of the near surface cover zone will be directly affected by the surrounding environment, and is the physical and chemical barrier protecting the steel reinforcement from potential corrosion. The carbonation process is also know to be affected by temperature, with increasing temperatures known to increase the carbonation rate (Roy et al, 1996).

7.4.1 Survey of Atmospheric Conditions in the UK

Figure 7.7 compares the atmospheric conditions throughout the UK. The temperature and precipitation figures are quite variable throughout the UK, with the South East having the highest temperatures and lowest precipitation. The western side of the country tends to have a greater deal of precipitation due to the prevailing weather conditions within the UK. The mean annual daily temperature varies from 7.5°C to around 11.0°C, however the precipitation is more widely varied with Northern Scotland experiencing almost 4 times as much precipitation as South East England. This difference in precipitation is likely to have an influence on the potential for carbonation and subsequent carbonation induced corrosion.

The atmospheric relative humidity is dependent on both temperature and the saturation vapour pressure of the atmosphere (Scorer, 1997). The amount of precipitation will influence the saturation vapour pressure and the mean atmospheric relative humidity was found to be higher in regions with greater precipitation. The western side of the UK appeared to be more humid, on average, than the eastern side, and this was mainly attributed to the precipitation figures.

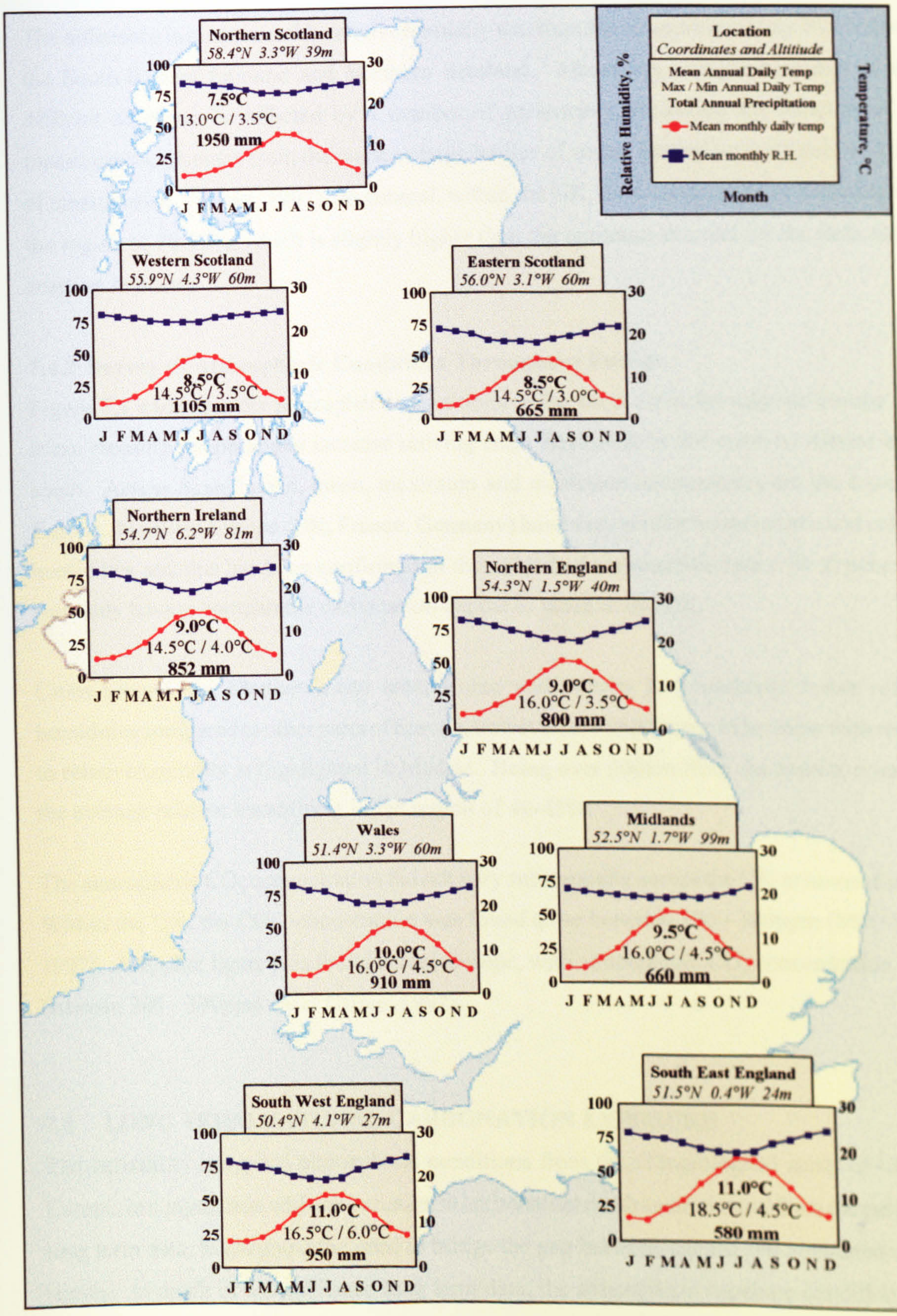


Figure 7.7 Comparison of typical atmospheric conditions within the UK (Data courtesy of UK Meteorological Office).

The difference in mean monthly relative humidity was found to be approximately 10% between the South-East of England and Northern Scotland. Measuring relative humidity is very difficult as it can be affected by a number of parameters, including the location of the measurement, distance from the coast or large bodies of water, ground temperature, and time of measurement (Scorer, 1997). In general, within the UK, the average relative humidity is in the region of 70-75%, which is slightly higher than the optimum deemed for the carbonation reaction to occur.

7.4.2 Survey of Atmospheric Conditions Throughout Europe

Figure 7.8 compares the atmospheric conditions in the main cities throughout Europe. The mean monthly temperatures increase moving from Reykjavik in the north to Athens in the south. Across Scandinavia, mean, maximum and minimum temperatures are the lowest in Europe. Northern Europe (UK, France, Germany) have very similar temperatures and relative humidities and this has been confirmed in the published carbonation data with structures in Germany having comparable carbonation depths to those in the UK.

Cities around the Mediterranean area, Rome and Athens had markedly lower relative humidities compared to other parts of Europe, however, the importance of location with respect to relative humidity is highlighted in Madrid. Being over 500km from the nearest coastline, the average relative humidity is in the region of 40-45%.

The atmospheric CO_2 concentration did not vary substantially across the UK or across Europe. Within the UK, the CO_2 concentration was found to be between 330 - 380ppm (Met Office, 1997). A similar figure was found across Europe, with atmospheric CO_2 concentration being between 340 - 390ppm (Met Office, 1997).

7.5 LONG TERM NATURAL CARBONATION EXPOSURE

The variability in typical atmospheric conditions from the climatological study of UK and Europe, in conjunction with the variation in carbonation depths experienced from the published long term data, highlighted the need to bridge the gap between natural and simulated natural testing. In much of the published long term data, the atmospheric exposure conditions were largely unknown and, in order to provide an exact comparison between concretes, all parameters including material characteristics, exposure conditions, and testing procedures must be clearly defined.

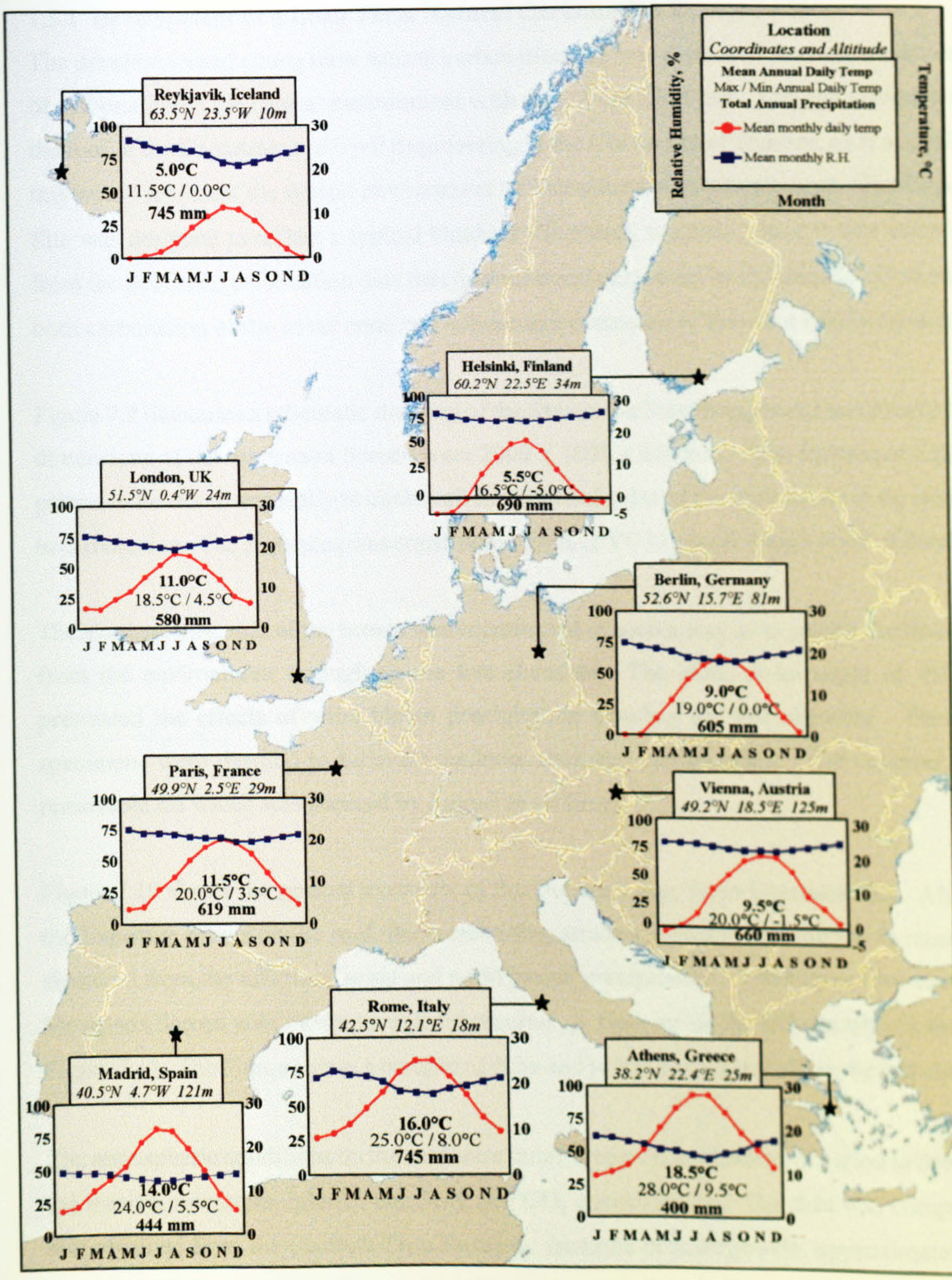


Figure 7.8 Comparison of typical atmospheric conditions throughout Europe (Data courtesy of www.weather-online.uk)

7.5.1 Development of a Long Term Natural Carbonation Exposure Site

The development of a long term natural carbonation site was proposed to compare the depths of carbonation in the natural environment with that of the CEN test. The site chosen was on the roof of the Department of Civil Engineering at the University of Dundee, as it was felt that this would represent the typical environment of a structural concrete element. The Exposure Site was designed to reflect a typical Outdoors Sheltered scenario, since it was established from the published carbonation data that this environment would be the most likely to support both carbonation of the cover zone and subsequent corrosion of the steel reinforcement.

Figure 7.9 illustrates a schematic drawing of the Stevenson Screen apparatus constructed. The dimensions of the Stevenson Screen were 2000 x 1000 x 650mm. This facilitated CEN test prisms to be stored vertically to enable all longitudinal sides of the specimens to be subjected to carbonation. The apparatus was constructed from uPVC to ensure a high level of durability.

The slatting at the side of the screen was constructed in such a way as to permit the flow of air from the environment throughout the test chamber. The slats, at an angle of 45°, also prevented the effects of wind blown precipitation entering the test chamber. Therefore, specimens were deemed to be in an outdoors sheltered environment. The chamber had a removable lid which was secured by screws at all times.

Figure 7.10 shows the general overview of the Dundee Long Term Exposure Site. Although the Exposure Site is on the roof, the surrounding structures ensure that the site is reasonably sheltered from the effects of wind and wind blown precipitation. The Figure also shows the Stevenson Screen with the removable lid secured. A view inside the test chamber is shown in Figure 7.11. The Figure shows a number of cube and prism specimens within the test chamber.

The atmospheric conditions on the roof were monitored over a month long period to determine the mean temperature, relative humidity and CO_2 concentration. The data was compared to that obtained from the Scottish Crop Research Institute at Invergowrie, approximately 2km from the Exposure Site. Figure 7.12 illustrates the changes in atmospheric conditions measured at the Dundee Long Term Exposure Site, and the Scottish Crop Research Institute (SCRI) data. A good correlation was found between the data with relative humidity being measured at approximately 70%. The temperature at the Dundee Exposure Site was measured over the period of the month of May and gave a similar mean temperature (approximately 12°C) to that of the SCRI data.

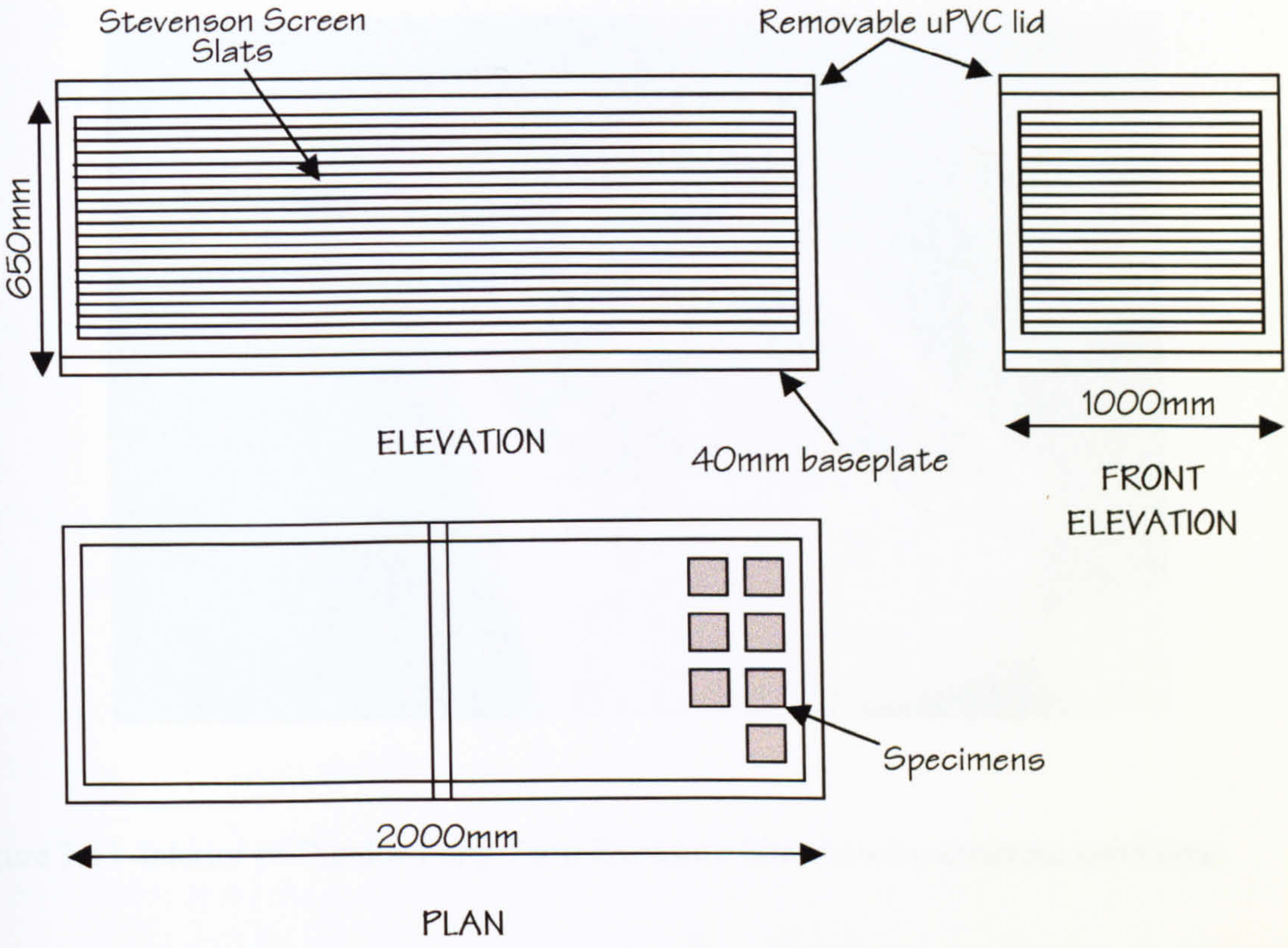


Figure 7.9 Schematic diagram of Stevenson Screen constructed for the Dundee Long Term Exposure Site.

Figure 7.10 General overview of Dundee Long Term Exposure Site

Figure 7.11 Interior of Dundee Long Term Exposure Site showing concrete specimens.

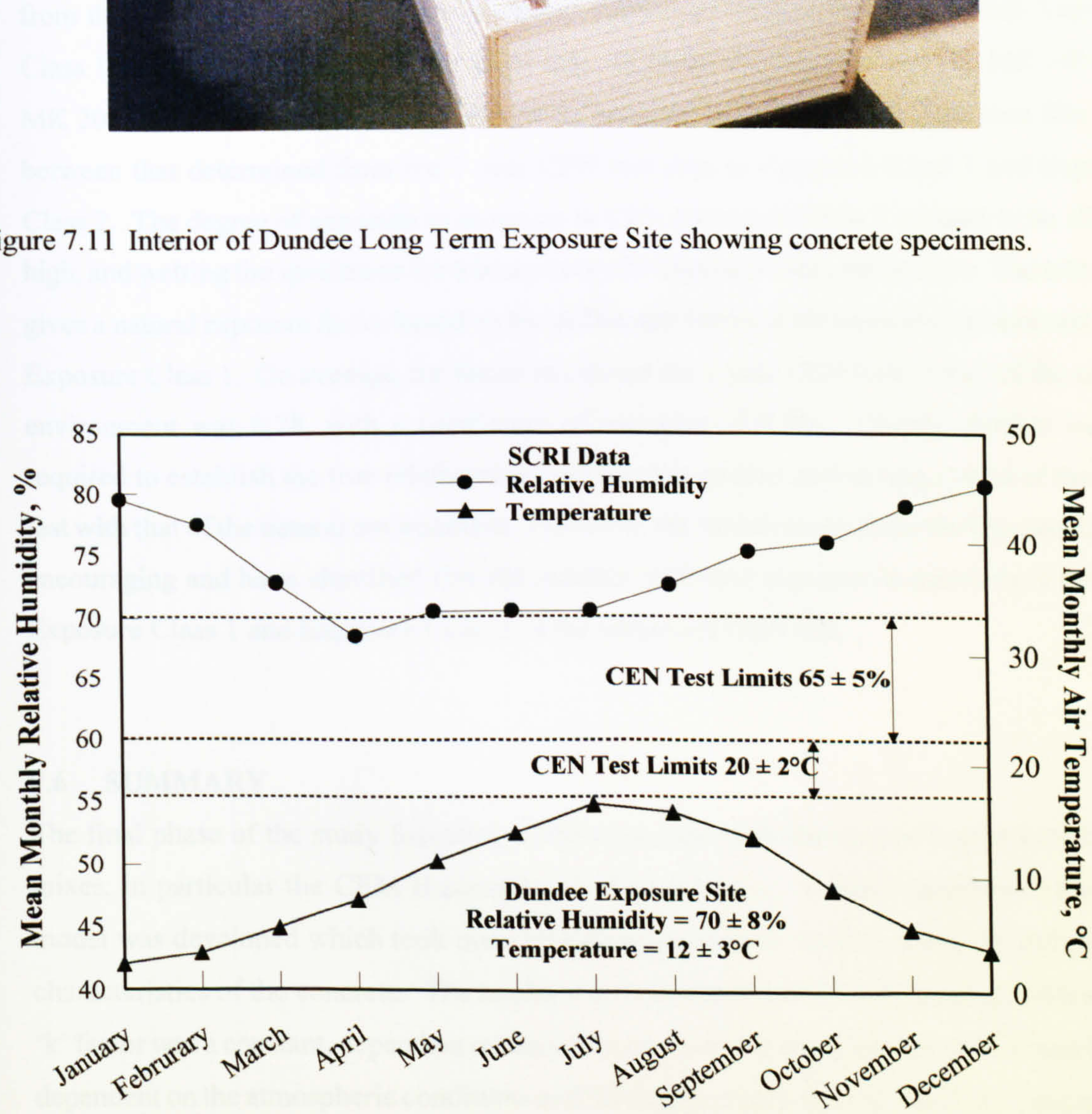


Figure 7.12 Comparison of typical atmospheric conditions measured at the Dundee Exposure Site with data from the Scottish Crop Research Institute (SCRI) at Invergowrie, approximately 2km from the Dundee site.

7.5.2 Comparison of Dundee Exposure Site 1 Year Data with CEN Test Data

Table 7.9 compares the carbonation depths measured at the Dundee Exposure Site with the data obtained at 1 year from the enhanced CEN carbonation test in Exposure Classes 1, 2 and 3. As with all concrete mixes in the study, the depths of carbonation were normalised for comparison on an equal strength basis of $f_{cm,28} = 37N/mm^2$. Curing procedures were similar to that of the CEN test with specimens being seal cured until $0.5f_{cm,28}$, before being transferred to the Exposure Site.

The data confirms the belief from the analysis of published long term data, and of that obtained from the CEN test, that the outdoor sheltered condition lies somewhere between Exposure Class 1 and Exposure Class 2 of the CEN test. With the exception of the PC, MK 10% and MK 20% mixes, the carbonation depths of the specimens in the Dundee Exposure Site were between that determined from the 1 year CEN test data in Exposure Class 1 and Exposure Class 2. The degree of exposure to moisture in CEN Exposure Class 2 appears to be slightly high, and wetting the specimens for 6 hours every 28 days prevents carbonation. The table also gives a natural exposure factor based on the difference between the natural exposure and CEN Exposure Class 1. On average, the factor to convert the 1 year CEN data to that of the natural environment was 0.78, with a coefficient of variation of 8.9%. Clearly, further work is required to establish the true relationship between the wetting and drying cycles of the CEN test with that of the natural environment. However, the initial results from the Dundee Site are encouraging and have identified that the outdoor sheltered exposure is somewhere between Exposure Class 1 and Exposure Class 2 of the enhanced CEN test.

7.6 SUMMARY

The final phase of the study focussed on the long term carbonation performance of the test mixes, in particular the CEM II concretes in Test Series 1. A multi regressive estimation model was developed which took into consideration the near surface chemical and physical characteristics of the concrete. The model was based on the $d=kt^n$ relationship, whereby the 'k' factor was a constant, dependant on the cover properties of the concrete, and 'n' was largely dependent on the atmospheric conditions and the degree of moisture to which the concrete was exposed. The 'n' values were based on the relationships formulated by non-linear regression of the CEN carbonation data up to a period of 2 years. For each Exposure Class in the CEN test, 'n' values were determined depending on the degree of wetting and drying to which the concrete was subjected.

Table 7.9 Comparison of 1 year carbonation data from the Dundee Exposure Site with that obtained from the CEN Test.

Mix[1]	1 Year Depth of Carbonation, mm				Natural / Simulated Natural Exposure Factor		
	Dundee Exposure Site	Simulated Natural Carbonation Test					
		Exposure Class 1	Exposure Class 2	Exposure Class 3	Class 1	Class 2	Class 3
PC/PFA 30%	3.0	4.0	2.5	1.5	**0.75**	**1.20**	**2.00**
PC	1.5	2.0	1.5	1.5	**0.75**	**1.00**	**1.00**
MK 10%	1.0	1.5	1.0	1.0	**0.67**	**1.00**	**1.00**
MK 15%	4.5	5.5	4.0	2.5	**0.81**	**1.13**	**1.80**
MK 20%	5.0	5.5	5.0	3.0	**0.90**	**1.00**	**1.67**
CSF 10%	4.0	5.5	3.0	2.5	**0.72**	**1.33**	**1.60**
CSF 15%	4.5	6.0	3.5	3.0	**0.75**	**1.29**	**1.50**
CSF 20%	5.5	6.5	4.0	2.5	**0.85**	**1.38**	**2.20**
				Mean	***0.78***	***1.16***	***1.60***
				σ	***0.07***	***0.16***	***0.43***
				V, %	***8.90***	***13.40***	***26.90***

[1] All mixes normalised to 37N/mm^2

The multi regressive model demonstrated a good correlation between the cover zone concrete properties and the depth of carbonation measured at 2 years. When carbonation depths were estimated to a period of 35 years, the water/PC ratio relationship, which had been determined in Chapter 5, was again observed. In Exposure Class 1, a limiting water/PC ratio of 0.65 was suggested for a compressive strength of 37N/mm^2. The water/PC ratio was increased in Exposure Class 2, and all mixes performed 'satisfactorily' in Exposure Class 2. The long term performance was based on the minimum cover requirements of BS8500-1:2001

Little correlation was noted between the CEN test results and those of the available published long term data. This was attributed to a number of reasons, including errors in the CEN test, errors in normalising the published data to a similar test strength and date, and the relatively large quantity of unknown variables in the published long term data, such as exact mix details and exposure conditions.

The inclusion of limestone filler in concrete had the potential to allow a trade-off between concrete quality and potential working life. An optimum level of 10% replacement of fine aggregate with limestone filler allowed a minimum reduction in the range of 2 - 10 N/mm^2 compressive strength and a 5-10mm reduction in cover, depending on the concrete type.

A comprehensive climatological study of typical UK and European atmospheric conditions revealed that relative humidity in the UK and Europe was generally outwith that of the CEN test limits of 65±5%. Temperatures also fluctuated, especially throughout Europe, with northern European Countries having lower temperatures and higher precipitation rates than those in Southern Europe. This highlighted the need for further analysis of the potential effects of macro and micro climate on carbonation of concrete structures.

Finally, a long term exposure site was initiated on the roof of the Department of Civil Engineering at the University of Dundee. A Stevenson Screen test chamber was constructed to replicate outdoor sheltered conditions. Carbonation depths measured at 1 year were similar to depths of carbonation between those measured in Exposure Class 1 and Exposure Class 2 of the CEN test. This indicated that the degree of wetting and drying in Exposure Class 2 is too frequent to represent outdoor sheltered exposure.

CHAPTER 8

CONCLUSIONS, PRACTICAL IMPLICATIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

8.1 INTRODUCTION

The emergence of a new set of European and British Standards for concrete practice in the past decade has led to the inclusion of a number of relatively unfamiliar cements now being permitted for use. The move towards a performance based specification in standards such as BS EN 206-1 and BS 8500 has increased the need for the development of suitable test methods to enable the performance of concrete to be judged under laboratory conditions. Determining the absolute performance of unknown materials under aggressive conditions is very important if the number of cements now permitted for use are to be confidently integrated into the UK and European concrete construction market.

The current study focussed on the development of a simulated natural carbonation test for hardened concrete to enable performance to be determined under laboratory conditions, with a view to comparing this performance with similar concretes in the field. The study also considered the durability of selected CEM II concretes containing metakaolin (MK) and condensed silica fume (CSF), which are currently less familiar to UK engineers but have the potential to be used in the near future. Given the nature of these unfamiliar cements, a physical and chemical study was undertaken to ascertain the dependency of carbonation on the cover zone concrete characteristics. The simulated natural test results were used to estimate long term carbonation performance by means of a multi-regressive model. This considers the initial physical and chemical characteristics of the concretes to ascertain whether the developed test method, in conjunction with the multi-regressive model, could be used to estimate long term carbonation performance under laboratory conditions.

The main conclusions at each phase of the study have been summarised at the end of each Chapter. This Chapter draws on the general conclusions of the study and underlines the practical implications arising from those conclusions. The chapter concludes with recommendations for future research.

8.2 OVERALL CONCLUSIONS

The key problems leading to the poor repeatability and reproducibility experienced in the European Round Robin of the draft CEN carbonation test were successfully identified. Analysis of the data showed that the variability in the Round Robin series was two-fold:

i) Many laboratories were unable to conform to the specified environmental test limits due to associated fluctuations in the natural laboratory conditions. Although temperature and relative humidity were reasonably easy to control, very few laboratories successfully simultaneously controlled temperature, relative humidity and CO_2 concentration.

ii) Different laboratories experienced difficulties in producing concrete with the desired workability due to variations in local materials. The corresponding concretes were not compared on an exact equal compressive strength basis, leading to variations in carbonation depth.

To overcome the variations in environmental conditions, the study proposed that the simulated natural carbonation test be carried out in a test chamber having active control over temperature, relative humidity, and CO_2 concentration. An in-house CO_2 monitoring and controller/injection system was developed to ensure the environmental parameters were kept within the recommended test limits of 300 ± 50ppm CO_2, 20 ± 2°C and 65 ± 5% RH.

A normalisation procedure was also proposed, whereby three mixes were cast to allow an exact interpolation of the mix parameters and performance at a specified compressive strength. This improved the reliability of the test for use as a comparative tool, which is particularly important when new materials are tested to a pass or fail criterion. This phase of the study concluded that the recommended developments improved the repeatability of the test and demonstrated that the test now had the potential to be reliably used in benchmarking concrete for performance in carbonating environments.

A statistical analysis of the carbonation data up to 2 years indicated that the relevant ranking of cement types changed up to period of 18 months. Therefore, it is recommended that the simulated natural carbonation test period be extended from 1 year to at least 1.5 years to ensure reliable results are obtained, and the relative ranking of performance is statistically significant and comparable.

The three CEN Exposure Classes reflected the effects of exposure to moisture on the depth of carbonation. Increasing the frequency of wetting and drying cycles reduced the depths of carbonation, and the degree of reduction in carbonation depth was found to be dependent on cement type. A thermogravimetric study of the concrete cover zone indicated that the wetting and drying cycles increased the degree of hydration in the outer 10mm of the concrete.

A study of selected CEM II binary concretes, containing PFA, condensed silica fume (CSF), and metakaolin (MK), determined the influence of both the chemical and physical characteristics of concrete in resisting carbonation. No single characteristic was found to govern carbonation resistance, however a good correlation was found between the near surface water vapour diffusivity and cover total calcium hydroxide. Selected concretes, such as those containing higher levels of MK and CSF, exhibited excellent near surface permeation properties. However, a reduced alkalinity in the cover zone meant that the carbonation front was able to progress at a relatively quick rate. The permeation and hydration study highlighted the caution required when specifying carbonation resistance of concrete on a single mix parameter, be it physical or chemical, and performance should be judged on a combination of both physical and chemical characteristics.

The parallel accelerated carbonation study also provided encouraging results. A reasonable correlation was found between 20 weeks accelerated and 2 year CEN carbonation, and it may be possible to tentatively gauge the long term performance of concrete from accelerated carbonation tests.

Closer inspection of the concrete mix proportions revealed that the water/PC ratio in the binary mixes is an influencing factor in carbonation resistance. Within a single compressive strength, it may be possible to specify a maximum water/PC ratio in order to resist carbonation. The water/PC ratio is one of the main forces behind the production of alkalinity in the concrete, which was identified as being a major factor in carbonation resistance. A tentative upper water/PC limit of 0.65 was recommended for 37N/mm^2 concrete.

The role of fine particles <125μm was investigated, and the packing densities of the mixes determined. Adjusting the fine/coarse aggregate ratio of the concrete was found to be detrimental to the concrete carbonation resistance. Examination of the physical packing of the mix constituents revealed that an excess of particles within a specific size range actually reduced the packing density of the concrete. The inclusion of a fine limestone filler, by means

of fractional replacement of the fine aggregate, was shown to improve the packing density and reduce the voids within the CEM II concretes. This was beneficial to the near surface permeation properties, and, across all cement types, an optimum fines content of 390-400kg/m^3, and an optimum limestone filler replacement level of 10% by weight of fine aggregate was proposed.

Varying the type of coarse aggregate did not directly affect the carbonation resistance of the concrete. However the coarse aggregate type did alter the mix proportions, permeation properties and potential cover alkalinity. This highlighted the caution that must be taken in specifying concrete mixes with varying coarse aggregate type.

The long term carbonation performance was estimated by means of a multi-regressive model which considered the physical and chemical characteristics of the cover zone concrete. Comparisons to published data proved difficult, and this was attributed to a number of reasons. The large number of unknown variables in the published data, such as exact mix proportions and exposure conditions, made it difficult to be certain that similar concretes were being compared. The Exposure Classes in the CEN did not appear to reflect those in the natural environment, and a long term natural exposure site was established. At 1 year, the results demonstrated that the an outdoor sheltered environment was equivalent to somewhere between Exposure Class 1 and Exposure Class 2 in the CEN test.

8.3 PRACTICAL IMPLICATIONS

The relentless shift in the philosophy towards specifying concrete by performance has stimulated research in the area of test development. The current study has made an important contribution in the development of a reliable simulated natural carbonation test to benchmark the performance of hardened concrete. The Exposure Classes now clearly defined in BS EN 206-1 and BS 8500 must be replicated under laboratory conditions in order to provide meaningful results, and the development of the current test method has determined that it may be possible to simulate outdoor exposure conditions by means of subjecting concrete to wetting and drying cycles.

A review of cement types which are now permitted in BS EN 197-1, but still unfamiliar to UK engineers, indicatedthat performance in a carbonating environment was dependent on both the physical and chemical properties of the cover zone concrete.

The permeation properties of the near surface zone influenced the carbonation rate of concrete, in particular, the water vapour diffusivity however, the chemical characteristics must also be considered.

In practical terms, measuring the near surface permeation and alkalinity of concrete can be a complicated and costly process. The current study demonstrated that the water/PC ratio of the concrete may potentially be used to determine carbonation performance of hardened concrete. Regardless of the non-Portland cement type and replacement level, the water/PC ratio was influencing the production of alkali material, namely $Ca(OH)_2$, in the cover zone. On an equal compressive strength basis, concretes with higher water/PC ratios generally had poorer carbonation resistance, even though permeation properties were similar. Across different cement types, the commonly used specification parameter, water/cement ratio, was found to have little influence. Although, within a cement type, the trends were similar, with increasing water/cement ratio providing increased carbonation depth. Across the cement types tested, all of which are permitted for use in BS EN 206-1 and BS 8500, there was no common trend towards a limiting water/cement ratio.

The performance of concrete in a carbonating environment may be improved through the partial replacement of fine aggregate with limestone filler. The physical characteristics of the mix constituents must be considered in order to maximise the benefits of improving the permeation properties of the concrete through the inclusion of a filler material. Replacement of the fine aggregate with filler improves the concrete cover physical properties without adversely affecting the chemical properties. Replacing the cementitious material with filler has the potential to reduce the alkalinity of the cover zone concrete and hence reduce the carbonation resistance.

Although the inclusion of a fine filler as a partial replacement of fine aggregate may increase the material cost of the concrete, the long term benefits in terms of improved carbonation resistance may actually lead to reductions in the whole life cost of structures. The improved carbonation resistance can, for instance, lead to a trade-off between concrete grade and cover depth for a specific minimum intended working life leading to lower overall material costs. The current study indicated that even up to a level of 15% replacement of fine aggregate with limestone filler, concrete grade and minimum cover depth can be reduced to achieve a similar intended working life of 50 years.

The optimum replacement level for the CEM II concretes tested was found to be 10%. The maximum level of filler permitted in BS EN 197-1 is now 5% unless the filler is considered part of the cementitious component of the concrete.

Estimating the long term performance of carbonation and comparing it to published long term data proved difficult. The shortcomings in comparting the data were attributed to the large quantities of unknown variables in the published data. Although, concretes were being compared on an equal strength basis, the study identified different carbonation depths, attributable to the variations in physical and chemical composition of the compared concretes. This highlighted the need for reliable field data, based on detailed historical records of the concrete, where possible. Details of the environment in which the concrete has performed must also be considered if a true comparison between laboratory based test methods and structures in the field is to be made, and absolute performance of concrete determined for specification purposes. The establishment of a long term exposure site in the current study showed that data can potentially be reliably transferred from natural to simulated natural conditions on test specimens

8.4 RECOMMENDATIONS FOR FUTURE RESEARCH

From the conclusions and practical implications arising from the current study, a number of areas may be further investigated. The following are suggestions for future research which could be carried out.

1. The simulated natural carbonation test developed should be subjected to a rigorous Round Robin test series similar to that carried out by CEN for the original draft test. This would determine the exact improvements to repeatability and reproducability of the enhanced test method, and determine its suitability for providing a reliable means of benchmarking unfamiliar concretes.

2. Initiation of a network of accurately monitored long term exposure sites to reflect the environmental conditions throughout the UK and Europe is required. This will allow a direct correlation to be established between the simulated natural conditions of the CEN test and those in the field. A refinement of the exact wetting and drying cycles required to replicate outdoor sheltered and outdoor unsheltered conditions should be established.

3. The suitability of a simulated natural carbonation test for determining the influences of material properties on carbonation-induced corrosion should be established. This may be integrated with a microstructural study of the concrete and the ways in which the pore structure and degree of moisture have the potential to affect carbonation and carbonation-induced corrosion.

4. The simulated carbonation test may also be further refined to include a multi aggressive cycle. A number of structures may be subjected to combined attack, for example carbonation and chloride attack. Therefore, a test method, combining Exposure Classes in BS EN 206-1 and BS 8500 to determine the effects of combined attack on concrete durability and, ultimately, utilised to benchmark performance, may be developed from the current test method.

5. Further investigation of the influence of the water/PC ratio on the carbonation resistance of concrete should be carried out. The fundamental relationship between the water/PC ratio and pore fluid chemistry should be investigated to determine it's exact effect on the carbonation process. Establishing a set of limiting water/PC ratios, with regard to concrete constituents, has the potential for specifying carbonation resistance on a water/PC ratio level. The work should include the effects of composite cements and ternary blends to test the hypothesis.

6. The multi-regressive model could be further refined to include the fundamental actions of carbon dioxide ingress through porous media, and the effects of micro and macro climate changes on carbonation. The effects of carbonation on the pore structure and climate changes, with respect to continuing pore refinement, may also be studied, with a view to providing a greater understanding of the carbonation process on the concrete microstructure.

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APPENDIX A

CEN METHOD FOR DETERMINATION OF THE RELATIVE CARBONATION PERFORMANCE OF A TEST CONCRETE AGAINST ONE OF ESTABLISHED CARBONATION PERFORMANCE

Original draft dated 26 June, 1995.

All recommended modifications from current study are given in red text.

1. AIM AND SCOPE

This laboratory method of testing consists of determining the depth of the carbonated layer on the surface of hardened concrete by means of an indicator under defined conditions.

The method is intended to be used for comparison of the behaviour of a concrete of established carbonation performance in practice with a concrete of unknown performance in combination with the (micro) climatic conditions.

Three conditioning classes are recommended for testing, the choice of the conditioning class being based on regional climate tests.

This recommendation does not cover the following:

a) initial type approval testing of concrete against absolute carbonation criteria;
b) in-situ carbonation testing.

2. DEFINITION

Carbon dioxide which penetrates the surface of concrete reacts with alkaline components in the cement paste. Once the reaction is complete the pH of the pore solution reduces to less than 9.

The reduction of the pH-value can be made visible by the colour change of a suitable indicator (this indicator method does not make it possible, however, to determine whether the reduction of the pH-value may have resulted from influences other than the absorption of CO_2 ; e.g. SO_2, HCl or other acidic gases). The depth of the reacted surface layer is called the depth of carbonation d_k.

3. PRINCIPLE

Two beams of a concrete of established carbonation performance (the reference concrete) and two beams of the test concrete are cast and sealed-cured until they reach 0.5 of their common compressive strength. They are then exposed to an atmosphere with normal levels of carbon dioxide and a temperature of 20° ± 2°C. At defined periods up to one year, slices are split from the beam and the freshly split surface sprayed with a phenolphthalein solution. The average depth of the reacted surface layer is measured and called the depth of carbonation. The results are expressed at a common compressive strength.

4. REAGENTS AND APPARATUS

4.1 A solution of 1% phenolphthalein in 70% ethyl alcohol.

4.2 A gauge to measure the depth of carbonation perpendicular to the surface with a precision of 0.5 mm.

4.3 A climate room with a temperature of 20°C ± 2°C, and relative humidity of 65% ± 5%.

4.4 Apparatus to maintain a CO_2 concentration within the climate room of 0.035% ± 0.005%.

4.5 Apparatus for recording with a precision of ±2.0 % R.H. and ±0.5° C.

4.6 Apparatus for recording CO_2 concentration [1] with a precision of ±0.001% by volume fitted with an audible/visual alarm to signify breaching of limits.

4.7 Standard table fans to facilitate circulation of air within the test chamber.

5. TESTING OF SPECIMENS

5.1 Specimens: type, making, curing and storage

The reference concrete should be specified or agreed. It should be one that is accepted as giving an acceptable performance in the place of use. In practice, the concretes that have acceptable performance will give a range of carbonation depths and it is recommended that the reference concrete should be one from the mid-range of carbonation depths e.g. a CEM II/B-V concrete.

The required consistence should be specified or agreed. The consistence should reflect that likely to be specified for the construction works.

Two test specimens of a concrete of established carbonation performance and two test specimens of a concrete of unknown performance are horizontally cast. Test prisms should be at least 400 mm long with a cross-section of 100 x 100 mm from which slices approximately 50 mm long can be split off, at each date of testing. In no case shall the shortest dimension of the prism be less than approximately 4 times the maximum nominal aggregate size. For each concrete to be tested, 3 mixes with constant free water content should be cast to allow the normalisation procedure detailed in Section 5.3 to be carried out:

- One primary mix containing the binder content judged to give the required strength.
- Two secondary mixes: one containing at least +8% binder content of the primary mix, and the other with at least -8% binder content of the primary mix.

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[1] Note: Some proprietary CO_2 controller systems contain a monitoring system to allow recording of CO_2 concentration.

The required strength should be specified or agreed. A suitable choice is the characteristic strength of the reference concrete i.e. the characteristic strength of a concrete with known acceptable performance. For example, if the durability provisions valid in the place of use require a C30/37 concrete, specify a cube strength of 37 MPa as the required strength. Alternatively convert the requirement for the maximum w/c ratio of the reference concrete into a characteristic strength.

Within each mix, six standard cubes/cylinders should be cast: three for strength testing to ascertain $0.5f_{cm,28}$ and three for strength testing at 28 days. During specimen preparation, it is important to avoid any unwanted effects on the concrete surface which could affect measurements. Therefore, the use of stripping agents should be kept to a minimum. Curing is as follows: 24 hours in the mould under a tentage of damp hessian and impermeable plastic sheeting. Immediately after demoulding the specimens are double wrapped in impermeable plastic film until their strength reaches 0.5 of their common compressive strength (seal cured). Note: The 0.5 of specimen common compressive strength has been selected as this equates to $0.5f_{cm,28}$, the curing requirement in ENV 13670-1: Execution of Concrete Works Part 1: General rules and rules for buildings.

One of the following storage classes should be selected or specified based on analysis of the regional climatic conditions.

- **Class 1:** storage at 20°C ± 2°C and 65% R.H. ± 5%;
- **Class 2:** storage at 20°C± 2°C and 65% R.H. ± 5% and after each 28 days wetting for 6 hours by placing the prisms under water;
- **Class 3**: storage at 20°C ± 2°C and 65% R.H. ± 5% and after each 7 days wetting for 6 hours by placing the prisms under water.

After immersion in water the specimens are stored outside the chamber at 20 ± 2°C and 65 ± 5% R.H. for 16 ± 2 hours to minimise any changes in relative humidity inside the chamber when they are returned. The mass before and after immersion is recorded along with the mass after the 16 ± 2 hour period.

The CO_2 content of the air within the storage room is required to be 0.035% ± 0.005% by volume. This is controlled by means of a CO_2 injector connected to the chamber room to replace CO_2 consumed by the carbonation reaction. A suitable apparatus is shown in Section 6 (Figure A.1). Monitoring of the readings from the CO_2 injection equipment should be carried out on a daily basis. Any deviations from this level should be reported. Standard mechanical table fans should be positioned within the test chamber to ensure circulation of air. It is recommended that the turbulence is monitored prior to the test specimens entering the chamber by means of a pigmented indicating air flow powder, or a similar method.

The water evaporation should be measured in the climate chamber by evaporation from a free deionised water surface and should be 55 ± 20 g/m²/hr. The evaporation is measured by mass loss from a deionised water filled evaporation bowl with a depth of approximately 40 mm and a cross sectional area of 225 ± 25 cm^2. The bowl shall be filled to 10 ± 1 mm from the brim. Accurate monitoring of the mass is recommended.

5.2 Testing

5.2.1 Testing age and generation of colour change

The following ages of testing for carbonation depth are required : 28, 91, 182, 273, 364 (± 2%) days after the sealed curing period as stated in Section 5.1, Paragraph 6.

A slice approximately 50 mm thick is broken off the beam for each test age. Depth of carbonation is measured on the freshly broken surface. Saw cuts are not suitable. Clear the broken surface immediately of dust and loose particles after breaking, and then spray with a fine mist of indicator solution. Avoid the formation of flow channels on the test surface. If only a weak colouration or none at all appears on the treated surface, repeat the spray test after ½ hour.

The measured depth of carbonation may be influenced by the time of measuring after application of the indicator solution therefore measurements should always be made approximately 1 hour after spraying.

In Class 2 or 3 conditioning where the date of carbonation measurement coincides with a wetting cycle, ensure carbonation measurement is performed prior to the wetting of the specimens.

5.2.2 Determination of the carbonation front

5.2.2.1 General

The carbonation front shall be determined by the colour change according to the method as stated below.

5.2.2.2 Measuring the depth of carbonation

The carbonation front shall be measured on five points on each face. To locate these points the edge length shall be divided into 8 equal distances. The 5 central points shall be used. With the help of a ruler or a sliding gauge the carbonation depth (d_k) shall be determined perpendicular to the surface of the beam with a precision of 0.5 mm per measured point.

The average carbonation depth is the arithmetical average of the five individual values, rounded to the nearest 0.5 mm. If the edges of the uncarbonated square are rounded off up to the outer measuring points, then use only the 3 central points.

5.2.2.3 Appreciation of dense aggregates

Dense aggregate that lies within the carbonation front will not be coloured by the phenolphthalein and the carbonation front will be interrupted by the grain, Figure 1a. For the determination of the carbonation depth, the theoretical carbonation front at the intersection of the location point and a line connecting the limits on each side of the grain, Figure 1b, shall be used.

5.2.2.4 Appreciation of pores, porous aggregates, and extreme values, d_k max

When there are pores or grains of porous aggregates lying in the area of the carbonation front, extreme values of the carbonation depth may appear, Figure 2. When the values of Δd_k are less than 4 mm they should be used in the calculation of the mean carbonation depth. Higher values of Δd_k should not be included when calculating the mean carbonation depth.

5.3 Normalisation Procedure

5.3.1 Stage 1 Normalisation of Carbonation Depths

For the three mixes cast, depth of carbonation is plotted against time up to 1 year as shown in Figure 3. At each test date the maximum d_k (excluding $\Delta d_k \geq 4$mm, see 5.2.2.4) , minimum d_k and the arithmetical mean of all included readings taken from the two prisms are plotted and the best fit regression line drawn.

5.3.2 Stage 2 Normalisation

From the compressive strength tests taken at 28 days the exact binder content to give a required strength can be determined by plotting cube/cylinder standard compressive strength against binder content, an example of which is shown in Figure 4a. The example given shows the initial primary mix having a binder content of 370 kg/m³ however to achieve the required standard compressive of 37N/mm², the binder content required is 374kg/m³. This is rounded to the nearest 5kg/m³ ie 375kg/m³.

Depth of carbonation from Figure 3 is plotted against binder content at all ages as shown in Figure 4b. From Figure 4a, the exact binder content is used on Figure 4b to record the subsequent depths of carbonation at the test dates for the test concrete mix at the required compressive strength. When reporting the results, all required binder contents are rounded to the nearest 5kg/m³. All depths of carbonation are rounded to the nearest 0.5mm.

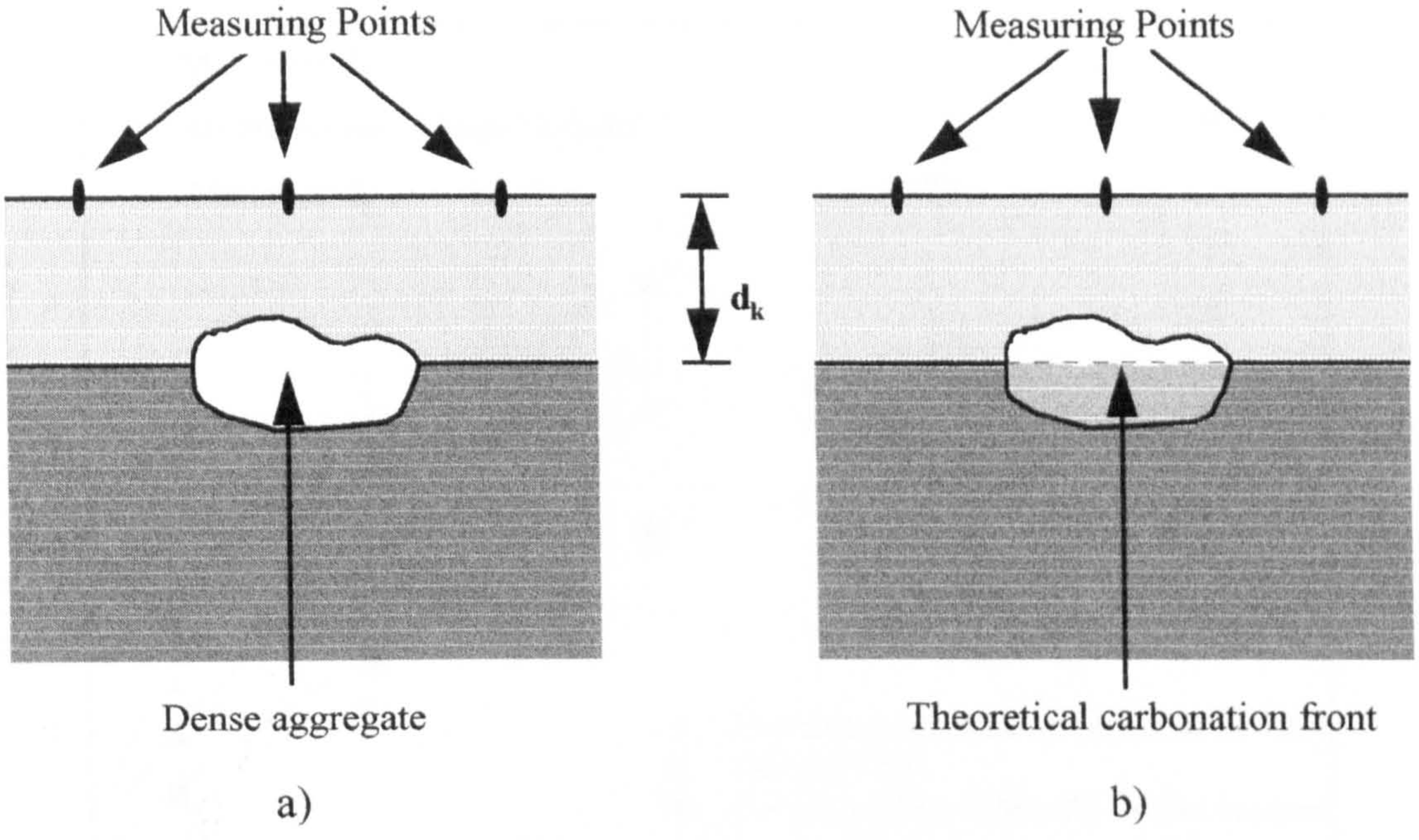


Figure 1 Procedure for obtaining the carbonation depth where the point falls within a dense aggregate particle. a) Dense aggregate interrupting carbonation front, b) theoretical carbonation front drawn across dense aggregate.

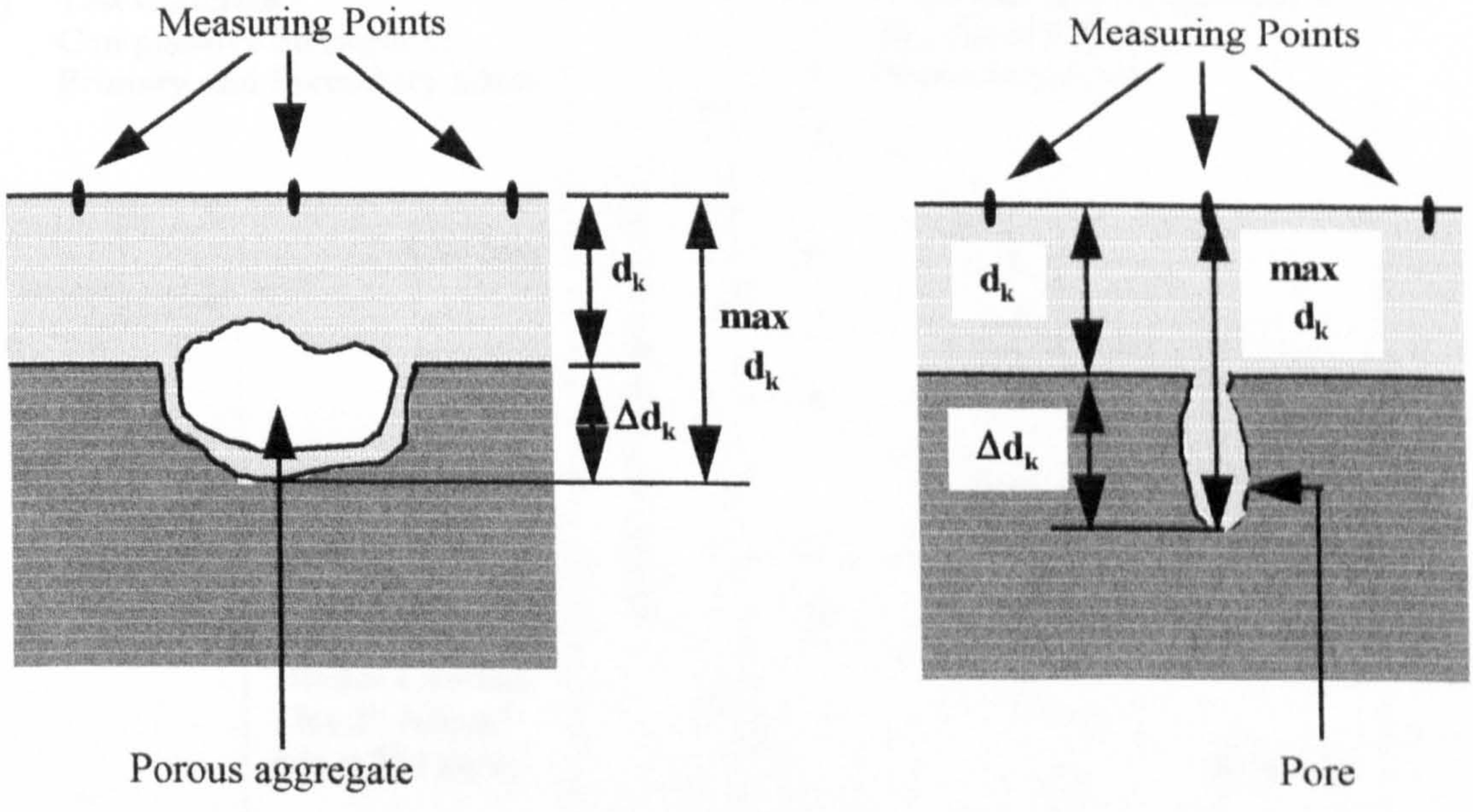


Figure 2 Procedure for obtaining the carbonation depth where the point falls on a porous aggregate particle or on an air void. Values of Δd_k greater than 4mm should not be used when calculating the average carbonation front.

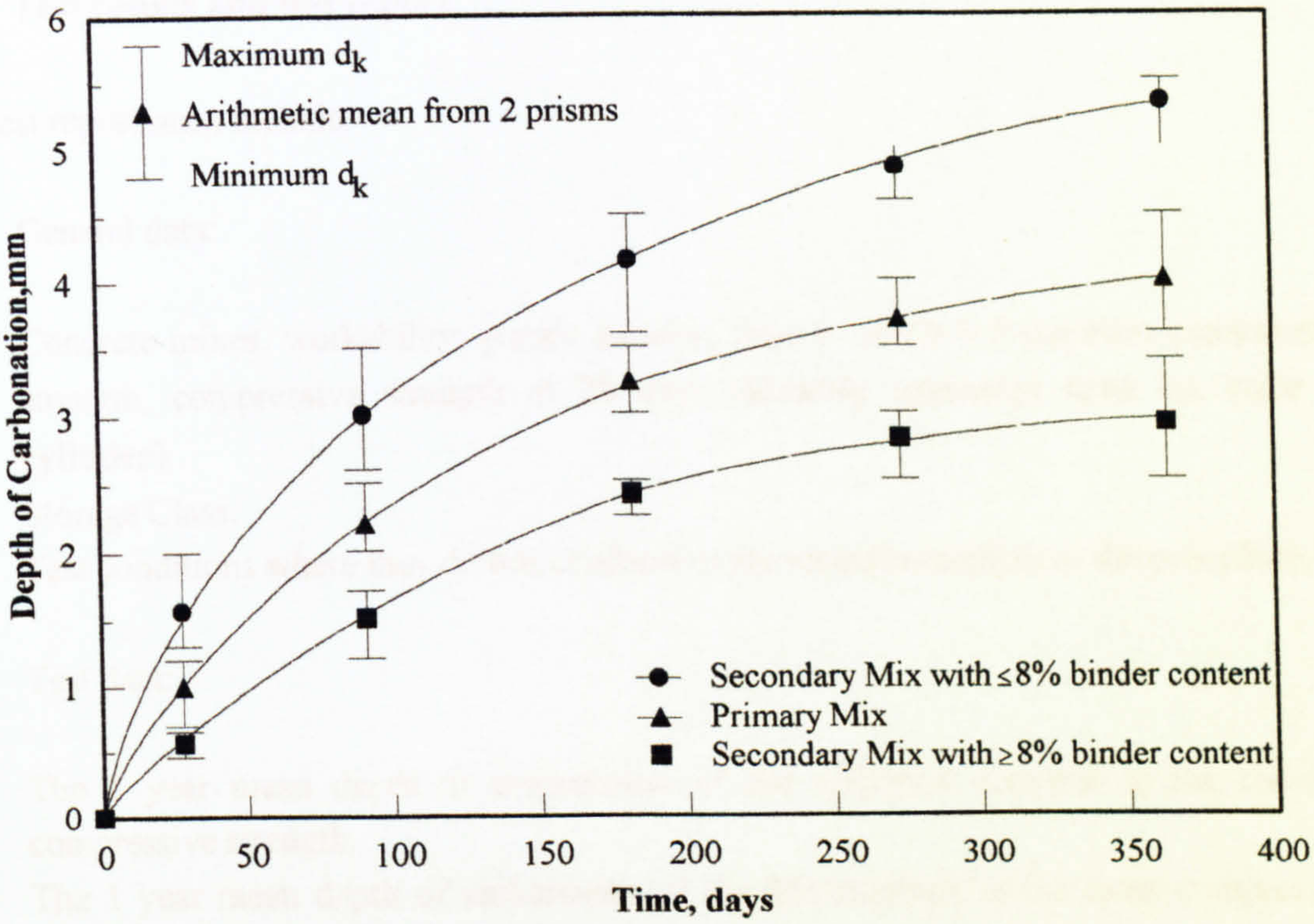


Figure 3 Example of Stage 1 normalisation for depth of carbonation up to 1 year.

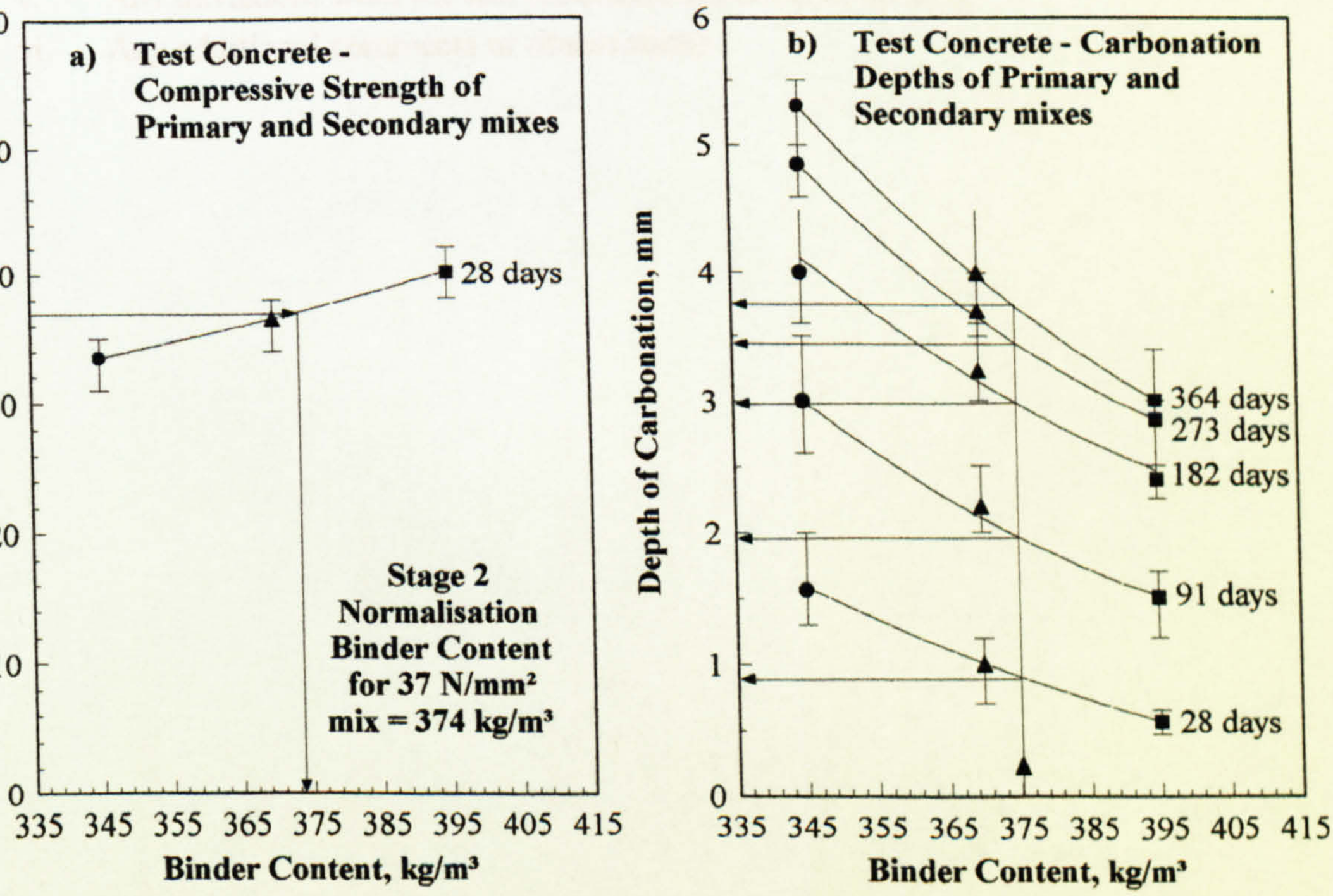


Figure 4 Example of Stage 2 normalisation. From Figure 4a the exact binder content to achieve the reference 28 day strength is found and rounded to the nearest 5kg/m³. From Figure 4b the subsequent depths of carbonation are recorded and rounded to the nearest 5mm.

5.4 Test results and test report

The test report must include:

a) General data:

i. Concrete mixes, workability, plastic density, time to reach 0.5 common compressive strength, compressive strength at 28 days **(identify specimen type i.e. cube or cylinder)**.
ii. Storage Class.
iii. Test conditions where they do not conform to the recommendation of the procedure.

b) Test data:

i. The 1 year mean depth of carbonation of the reference concrete at the required compressive strength.
ii. The 1 year mean depth of carbonation of the test concrete at the same compressive strength.
iii. Figures 3 and 4.
iv. Where requested, some or all of the data given in the completed forms, see Section 7.
v. Any deviations from the test procedure not covered by a) iii.
vi. Any additional comments or observations.

SECTION 6

Line Diagram of a suitable CO_2 Injection System

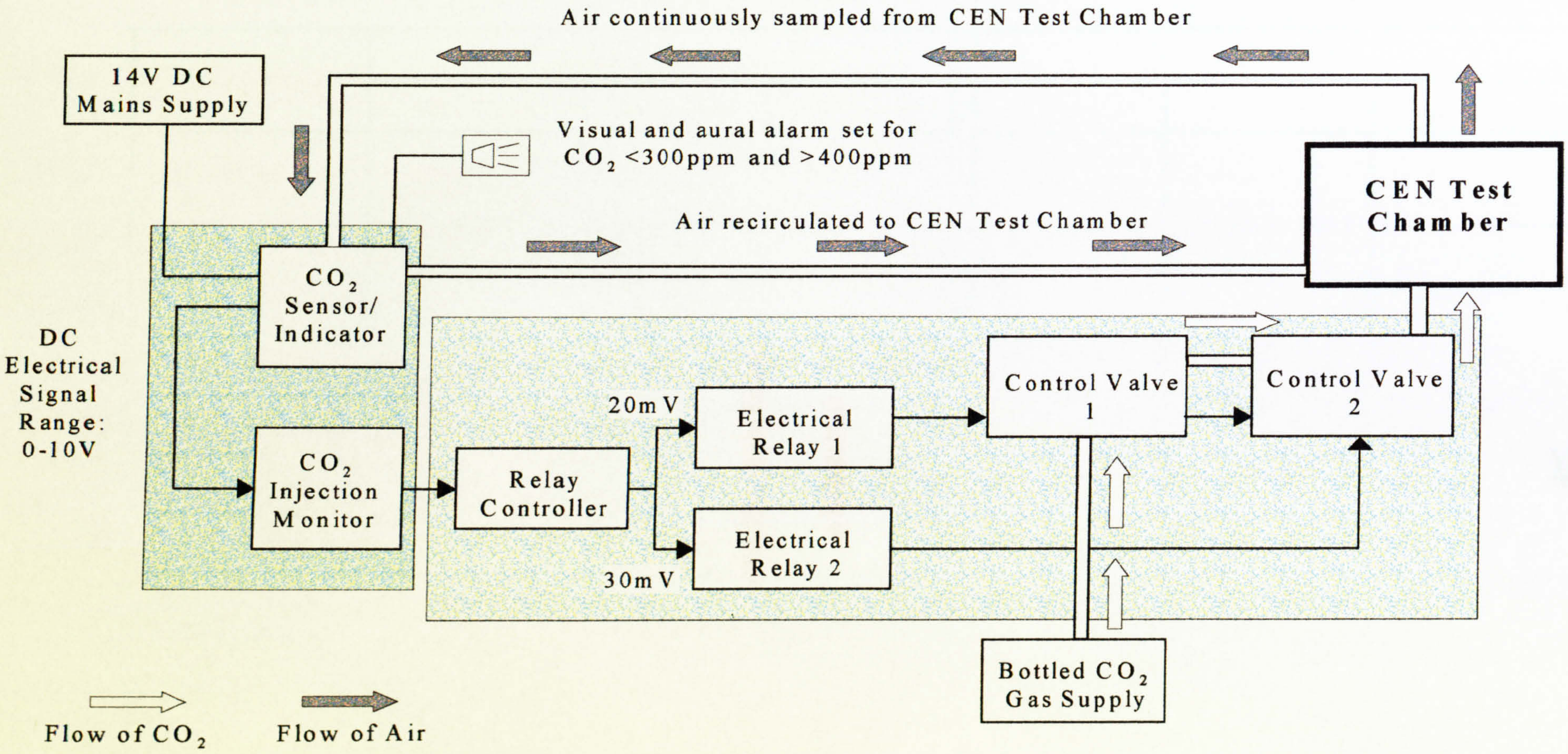


Figure A1 Typical schematic diagram of CO_2 injection and monitoring system.

SECTION 7

Summary of Test Data

Table A1 Summary of Carbonation Depth Test Data.

Storage Class	Reference Concrete									Test Concrete								
	- 8% Binder			Primary Mix			+ 8% Binder			- 8% Binder			Primary Mix			+ 8% Binder		
Test Duration, days	Average [1] 1	2	Mean	Average [1] 1	2	Mean	Average [1] 1	2	Mean	Average [1] 1	2	Mean	Average [1] 1	2	Mean	Average [1] 1	2	Mean
28 ± 2%																		
91 ± 2%																		
182 ± 2%																		
273 ± 2%																		
364 ± 2%																		

[1] Note: Indicate where the average depth of carbonation is not the average of 20 readings.

Table A2 Summary of Compressive Strength Test Data.

28 day Compressive Strength Data		
Specimen Type: (i.e. Cube or cylinder?)		
Reference Concrete: -8% binder content	=	MPa
Reference Concrete: Primary Mix	=	MPa
Reference Concrete: +8% binder content	=	MPa
Test Concrete: -8% binder content	=	MPa
Test Concrete: Primary Mix	=	MPa
Test Concrete:+8% binder content	=	MPa

APPENDIX B

Stage 1 Normalisation data for Test Series 1 mixes:

Compressive strength, Permeation and Carbonation Test Data

Example of Statistical Analysis of Distribution of Carbonation Depths

1 Year CEN Carbonation Specimens

Table B.1 Stage 1 Normalisation Compressive Strength data for Series 1 mixes.

Mix	Cement Content kg/m³	Test Date, days									2/28 day ratio
		2	3	7	14	28	60	90	180	364	
PFA	345	11.0	16.5	23.0	28.0	*33.5*	42.0	44.5	47.5	49.5	**0.33**
	370	12.5	18.5	25.5	30.5	*36.5*	44.5	47.5	50.5	52.0	**0.34**
	395	16.0	21.0	28.5	34.0	*40.0*	47.5	50.5	53.5	55.0	**0.40**
PC	290	12.0	18.0	25.5	30.5	*34.5*	37.0	38.0	39.0	43.0	**0.35**
	315	14.5	21.0	30.0	35.5	*40.0*	42.5	43.5	44.5	46.0	**0.36**
	340	18.0	25.0	35.0	41.5	*46.0*	48.0	49.0	50.0	52.0	**0.39**
MK 10%	280	16.5	18.5	22.0	26.5	*32.0*	34.5	35.0	36.0	38.0	**0.52**
	305	19.0	21.5	25.5	30.5	*35.5*	38.0	38.5	39.5	42.0	**0.54**
	330	22.0	25.5	31.0	35.5	*39.5*	42.0	42.5	43.5	45.0	**0.56**
MK 15%	270	11.5	14.5	22.5	29.5	*35.5*	38.0	38.5	40.0	41.0	**0.32**
	295	13.5	17.0	24.5	31.5	*38.0*	40.5	40.5	41.5	43.0	**0.36**
	320	17.0	20.5	29.5	36.0	*41.5*	43.5	44.0	44.5	46.0	**0.41**
MK 20%	265	9.5	12.5	21.0	28.5	*34.5*	36.0	36.0	37.0	42.0	**0.28**
	290	12.0	15.5	24.5	33.0	*39.0*	40.5	41.0	42.0	46.0	**0.31**
	315	16.0	19.5	29.0	38.5	*44.5*	46.0	46.5	47.5	49.0	**0.36**
CSF 10%	260	10.0	13.5	21.0	27.5	*34.5*	39.0	40.5	41.5	43.0	**0.29**
	285	13.0	16.5	24.5	31.0	*38.0*	43.0	45.0	46.0	48.0	**0.34**
	310	17.0	21.0	29.0	36.0	*42.5*	47.5	49.0	50.5	51.0	**0.40**
CSF 15%	280	16.5	22.0	28.5	35.0	*37.0*	42.5	46.0	49.5	50.0	**0.45**
	305	17.0	23.5	29.5	38.0	*41.5*	44.5	48.0	50.5	52.0	**0.45**
	330	19.0	25.5	30.0	41.0	*44.0*	47.0	49.0	52.5	53.0	**0.43**
CSF 20%	280	15.0	21.0	27.0	28.5	*35.5*	37.0	39.0	42.0	44.0	**0.42**
	305	17.0	22.5	27.0	36.0	*39.5*	41.5	43.5	44.0	46.0	**0.43**
	330	20.5	24.5	28.5	38.0	*42.0*	43.0	45.0	48.0	51.0	**0.48**

Table B.2 Stage 1 Normalisation Initial Surface Absorption Test data for Series 1 mixes.

Mix	Binder Content, kg/m³	ISA 10, ml/m²/s x 10^{-2}				ISA n value			
		Pre-entry	182d	364d	728d	Pre-entry	182d	364d	728d
PFA 30%	345	60.0	47.5	40.7	38.9	0.32	0.33	0.33	0.34
	370	56.0	43.7	38.6	36.5	0.35	0.36	0.37	0.37
	395	53.0	41.8	36.9	35.7	0.36	0.37	0.39	0.39
PC	290	68.9	57.3	51.1	48.5	0.30	0.32	0.34	0.35
	315	57.5	47.1	42.0	40.1	0.33	0.36	0.38	0.38
	340	54.1	43.4	38.6	37.0	0.37	0.39	0.41	0.41
MK 10%	280	45.2	41.7	38.9	36.4	0.40	0.42	0.43	0.43
	305	36.4	34.6	33.3	32.4	0.43	0.45	0.46	0.47
	330	33.4	32.2	31.2	29.2	0.47	0.49	0.50	0.51
MK 15%	270	50.4	39.6	31.0	28.9	0.41	0.43	0.44	0.45
	295	44.9	34.2	27.0	24.6	0.43	0.45	0.47	0.48
	320	42.8	33.1	24.7	23.0	0.45	0.47	0.49	0.49
MK 20%	265	48.7	37.0	27.1	24.2	0.44	0.46	0.47	0.48
	290	44.0	33.3	24.7	21.4	0.47	0.48	0.49	0.50
	315	42.9	32.3	24.0	19.6	0.49	0.51	0.53	0.54
CSF 10%	260	52.3	37.0	32.0	25.6	0.42	0.43	0.44	0.45
	285	41.2	26.9	24.1	20.1	0.44	0.46	0.47	0.48
	310	35.5	22.5	20.7	19.0	0.45	0.46	0.47	0.48
CSF 15%	280	47.2	29.4	21.4	19.9	0.44	0.45	0.46	0.48
	305	31.0	18.7	15.4	13.4	0.45	0.47	0.48	0.49
	330	27.1	16.2	14.2	12.4	0.47	0.48	0.48	0.49
CSF 20%	280	46.2	28.4	20.1	18.9	0.44	0.46	0.46	0.48
	305	30.0	18.5	15.2	13.5	0.46	0.47	0.48	0.49
	330	25.1	17.2	13.1	10.5	0.47	0.47	0.48	0.49

Table B.3 Stage 1 Normalisation Intrinsic Air Permeability and Capillary Absorption data for Series 1 mixes.

Mix	Binder Content, kg/m³	Intrinsic Air Permeability, m^2x10^{-17}				Capillary Porosity, %			
		Pre-entry	182d	364d	728d	Pre-entry	182 d	364d	728d
PFA 30%	345	43.1	29.4	23.3	21.4	5.9	5.3	4.8	4.5
	370	36.3	25.4	20.3	17.0	4.9	4.5	4.3	4.2
	395	31.8	24.2	19.0	16.5	4.5	4.3	4.1	3.8
PC Bulk	290	67.4	57.5	52.4	50.2	6.3	5.8	5.6	5.4
	315	51.5	45.5	43.1	42.0	5.5	5.4	5.3	5.0
	340	47.5	42.6	40.3	38.1	5.0	4.8	4.6	4.5
MK 10%	280	26.1	23.9	19.7	15.6	7.0	5.8	5.4	5.4
	305	18.7	15.0	13.8	12.4	6.0	5.0	4.9	4.7
	330	13.3	11.4	10.7	10.0	5.7	4.8	4.6	4.4
MK 15%	270	25.7	21.0	15.2	14.3	6.8	5.5	5.4	4.9
	295	18.7	13.1	11.1	10.6	5.7	4.6	4.5	4.2
	320	14.3	11.4	10.0	9.4	5.4	4.5	4.4	4.0
MK 20%	265	29.5	20.4	15.2	14.2	7.3	5.4	4.8	4.5
	290	21.0	14.2	11.4	11.0	5.9	4.8	4.4	4.1
	315	15.8	12.0	10.2	9.8	5.4	4.6	4.3	3.9
CSF 10%	260	25.6	20.7	14.5	11.4	6.9	5.5	5.2	4.9
	285	16.2	12.0	8.6	8.2	5.9	4.9	4.7	4.5
	310	13.3	9.9	8.1	7.9	5.6	4.6	4.5	4.3
CSF 15%	280	21.4	13.8	10.8	9.7	6.7	5.8	5.3	5.2
	305	16.8	10.3	8.1	8.0	6.0	5.0	4.7	4.6
	330	15.1	9.3	7.3	7.0	5.7	4.7	4.5	4.4
CSF 20%	280	21.5	13.8	10.8	10.1	5.7	5.8	5.3	5.0
	305	15.9	12.3	8.6	8.2	6.0	5.0	4.7	4.5
	330	14.0	9.5	7.9	7.5	5.7	5.7	4.5	4.0

Table B.4 Stage 1 Normalisation Coefficient of Water Vapour Diffusivity data for Series 1 mixes.

Mix	Binder Content, kg/m³	Coefficient of Water Vapour Diffusivity, x 10^{-10} g/mm s mm Hg							
		0-25 mm cover depth				25-50mm cover depth			
		Pre-entry	182d	364d	728d	Pre-entry	182d	364d	728d
PFA 30%	345	114.3	101.9	90.6	89.1	110.7	85.1	51.4	50.6
	370	112.3	100.2	88.3	86.1	108.8	77.2	48.0	47.6
	395	111.4	99.2	86.7	84.2	101.4	73.2	46.4	45.2
PC	290	198.5	178.8	161.9	157.2	193.2	143.6	127.3	120.9
	315	181.1	164.9	152.4	148.6	175.6	124.7	112.8	108.4
	340	172.5	158.3	149.1	143.4	167.3	118.1	108.4	100.6
MK 10%	280	99.6	86.9	77.6	72.1	90.8	50.7	32.0	31.4
	305	58.3	53.4	50.4	45.6	59.0	34.2	24.6	23.9
	330	45.1	43.3	41.6	38.2	44.1	26.0	19.7	18.9
MK 15%	270	79.9	70.6	62.3	58.1	90.8	65.6	53.0	50.4
	295	55.9	51.3	48.2	42.4	59.0	41.9	33.2	32.9
	320	49.3	43.3	41.6	38.6	49.0	34.2	26.6	24.9
MK 20%	265	78.9	70.6	62.3	58.9	86.9	71.1	60.7	55.2
	290	53.9	51.3	48.2	43.4	66.7	55.3	46.4	45.9
	315	47.3	43.3	42.4	37.4	56.3	47.9	40.9	38.0
CSF 10%	260	84.6	66.8	54.4	42.9	86.9	71.1	52.3	50.8
	285	51.9	41.6	36.1	33.7	50.8	37.0	32.0	31.4
	310	40.1	34.6	32.2	30.8	38.5	28.1	26.1	25.2
CSF 15%	280	73.2	46.5	41.1	36.9	68.6	56.8	47.9	44.9
	305	44.5	30.7	27.2	24.8	44.9	39.5	32.0	30.5
	330	40.1	27.7	25.7	20.2	36.0	31.5	26.1	25.0
CSF 20%	280	72.0	46.5	41.1	36.9	68.6	55.6	48.9	45.8
	305	43.1	30.3	26.3	23.6	43.8	39.1	31.5	31.5
	330	41.1	29.7	24.5	20.2	36.5	32.5	25.2	23.6

Table B.5 Stage 1 Normalisation carbonation depths for Series 1 mixes.

Mix	CEN Exposure Class	Binder Content, kg/m³	Mean Depth of Carbonation from 2 prisms, mm						
			28d	91d	182d	273d	364d	546d	728d
PFA 30%	1	345	1.5	3.0	4.0	5.0	5.5	6.0	6.5
		370	1.0	2.0	3.0	3.5	4.0	4.5	5.0
		395	0.5	1.5	2.5	3.0	3.0	3.5	4.0
	2	345	1.5	2.5	3.0	3.5	4.0	4.5	5.0
		370	0.5	2.0	2.0	2.5	2.5	3.0	3.5
		395	0.0	1.0	1.5	1.5	1.5	2.0	2.5
	3	345	1.0	1.5	2.0	2.5	2.5	3.0	3.5
		370	0.5	1.0	1.5	1.5	2.0	2.5	3.0
		395	0.0	0.5	1.0	1.0	1.0	1.5	2.0
PC	1	290	0.5	1.0	2.0	2.0	2.5	3.0	3:5
		315	0.5	1.0	1.0	1.5	1.5	2.0	2.5
		340	0.0	0.5	1.0	1.0	1.5	2.0	2.0
	2	290	0.5	1.0	1.5	2.0	2.0	2.5	2.5
		315	0.0	0.5	1.0	1.0	1.0	1.5	2.0
		340	0.0	0.5	0.5	0.5	1.0	1.5	1.5
	3	290	0.5	1.0	1.0	1.5	1.5	2.0	2.5
		315	0.0	0.5	0.5	1.0	1.0	1.5	2.0
		340	0.0	0.0	0.5	0.5	0.5	1.0	1.5
MK 10%	1	280	1.0	1.5	2.5	3.0	3.0	3.5	4..0
		305	0.5	1.0	1.5	2.0	2.0	2.5	3.0
		330	0.5	0.5	1.0	1.0	1.5	2.0	2.5
	2	280	1.0	1.5	2.0	2.5	2.5	3.0	3.5
		305	0.5	1.0	1.0	1.5	1.5	2.0	2.5
		330	0.0	0.5	0.5	0.5	0.5	1.0	1.5
	3	280	0.5	1.0	1.0	1.5	1.5	2.0	2.5
		305	0.0	0.5	0.5	1.0	1.0	1.5	2.0
		330	0.0	0.0	0.5	0.5	0.5	1.0	1.5
MK 15%	1	270	2.0	4.0	5.0	5.5	6.5	7.5	8.0
		295	1.5	3.0	3.5	4.5	5.0	5.5	7.0
		320	1.0	2.0	3.0	3.5	3.5	4.5	5.5
	2	270	1.5	3.0	4.0	4.5	5.0	5.5	6.0
		295	1.0	2.0	3.0	3.0	3.0	3.5	4.0
		320	0.5	1.5	2.0	2.0	2.0	3.0	3.5
	3	270	0.5	1.5	2.5	3.0	3.0	3.5	4.0
		295	0.5	1.0	1.5	2.0	2.0	2.5	3.0
		320	0.0	0.5	1.0	1.0	1.0	1.5	2.0

Table B.6 Stage 1 Normalisation carbonation depths for Series 1 mixes (contd.).

Mix	CEN Exposure Class	Binder Content, kg/m³	Mean Depth of Carbonation from 2 prisms, mm						
			28d	91d	182d	273d	364d	546d	728d
MK 20%	1	265	2.5	4.0	5.5	6.5	7.0	7.5	8.0
		290	1.5	3.0	4.0	5.0	5.0	5.5	6.0
		315	1.0	2.5	3.5	4.0	4.0	4.5	5.0
	2	265	2.0	3.5	4.5	5.5	6.0	7.0	7.5
		290	1.5	2.5	3.5	4.0	4.5	5.0	5.5
		315	1.0	1.5	2.5	3.0	3.5	4.0	4.5
	3	265	1.0	2.0	3.0	3.5	4.0	4.5	5.0
		290	0.5	1.0	2.0	2.0	2.5	3.0	3.5
		315	0.0	0.5	1.0	1.5	1.5	2.0	2.5
CSF 10%	1	260	2.5	4.0	5.0	6.0	6.5	7.5	8.0
		285	2.0	3.0	4.5	5.0	5.5	6.0	6.5
		310	1.5	2.5	3.5	4.5	4.5	5.0	5.5
	2	260	1.5	2.5	3.5	3.5	4.0	4.5	5.0
		285	1.0	2.0	2.0	2.5	2.5	3.0	3.5
		310	0.5	1.0	1.5	2.0	2.0	2.5	3.0
	3	260	1.0	2.0	3.0	3.5	3.5	3.5	4.0
		285	0.5	1.5	2.0	2.0	2.0	2.5	3.0
		310	0.5	1.0	1.0	1.5	1.5	2.0	2.5
CSF 15%	1	280	2.0	3.5	4.5	5.5	6.5	7.0	7.5
		305	1.0	2.5	3.5	4.0	4.5	5.0	5.5
		330	0.5	2.0	2.5	3.0	3.5	4.0	4.5
	2	280	1.5	2.5	3.5	3.5	4.0	4.5	5.0
		305	1.0	2.0	2.0	2.5	2.5	3.0	3.5
		330	0.5	1.0	1.5	2.0	2.0	2.5	3.0
	3	280	1.0	1.5	2.5	3.0	3.0	3.5	4.0
		305	0.5	1.0	1.5	1.5	2.0	2.5	3.0
		330	0.0	0.5	1.0	1.0	1.0	1.5	2.0
CSF 20%	1	280	2.0	3.5	4.5	5.5	6.5	7.0	7.5
		305	1.0	2.5	3.5	4.0	4.5	5.0	5.5
		330	0.5	2.0	2.5	3.0	3.5	4.0	4.5
	2	280	1.5	2.5	3.5	3.5	4.0	4.5	5.0
		305	1.0	2.0	2.0	2.5	2.5	3.0	3.5
		330	0.5	1.0	1.5	2.0	2.0	2.5	3.0
	3	280	1.0	1.5	2.5	3.0	3.0	3.5	4.0
		305	0.5	1.0	1.5	1.5	2.0	2.5	3.0
		330	0.0	0.5	1.0	1.0	1.0	1.5	2.0

Table B.7 Example of fitting a normal curve to distributed data and testing 'goodness of fit' by means of a Chi-squared test.

Fitting a normal curve to CEN 1 year carbonation data								Testing "goodness of fit" of normal curve using Chi-squared (χ^2) test			
Depth of Carbonation interval, mm	Observed Frequency, O	Upper Limit of Interval, a	x=a-$\bar{x}$	Standard Result z=(x/σ)	Proportion of Normal Curve		Expected Frequency, E cxN	Adjusted[4] Frequency		$\chi^2 = \Sigma \frac{(O-E)^2}{E}$	Corrected for Yates[5] Continuity, χ^2_{corr}
					Below[1] Interval, b	Within[2] Interval, c		O	E		
6.5-6.9	1	6.95	2.85	2.82	0.9967	0.0066	0.3	-	-	-	-
6.0-6.4	1	6.45	2.35	2.33	0.9901	0.0237	0.9	-	-	-	-
5.5-5.9	3	5.95	1.85	1.83	0.9664	0.0565	2.3	-	-	-	-
5.0-5.4	4	5.45	1.34	1.34	0.9099	0.1104	4.4	10	7.9	0.56	0.32
4.5-4.9	8	4.95	0.85	0.84	0.7995	0.1612	6.4	7	6.4	0.05	0.00
4.0-4.4	9	4.45	0.35	0.35	0.6383	0.1979	7.9	9	7.9	0.15	0.04
3.5-3.9	6	3.95	-0.15	-0.15	0.4404	0.1793	7.2	5	7.2	0.66	1.00
3.0-3.4	4	3.45	-0.65	-0.64	0.2611	0.1340	5.4	4	5.4	0.35	0.65
2.5-2.9	3	2.95	-1.15	-1.14	0.1271	0.0853	3.4	5	5.1	0.00	0.07
2.0-2.4	1	2.45	-1.75	-1.73	0.0418	0.0418	1.7	-	-	-	-
Total, N	**40**						$\Sigma = 39.9$[3]				$\Sigma = 2.08$
Mean, $\bar{x}$	**4.1**										
S.Dev, σ	**1.01**										

In this case at a 95% confidence level, $\chi^2 = 2.167^*$ thus the difference between the observed and expected frequency is insignificant. Thus we can deduce that the data is normally distributed.

[1] Proportion of the area of normal curve* below the interval in column 1.

[2] Proportion of the area of normal curve* within interval in column 1.

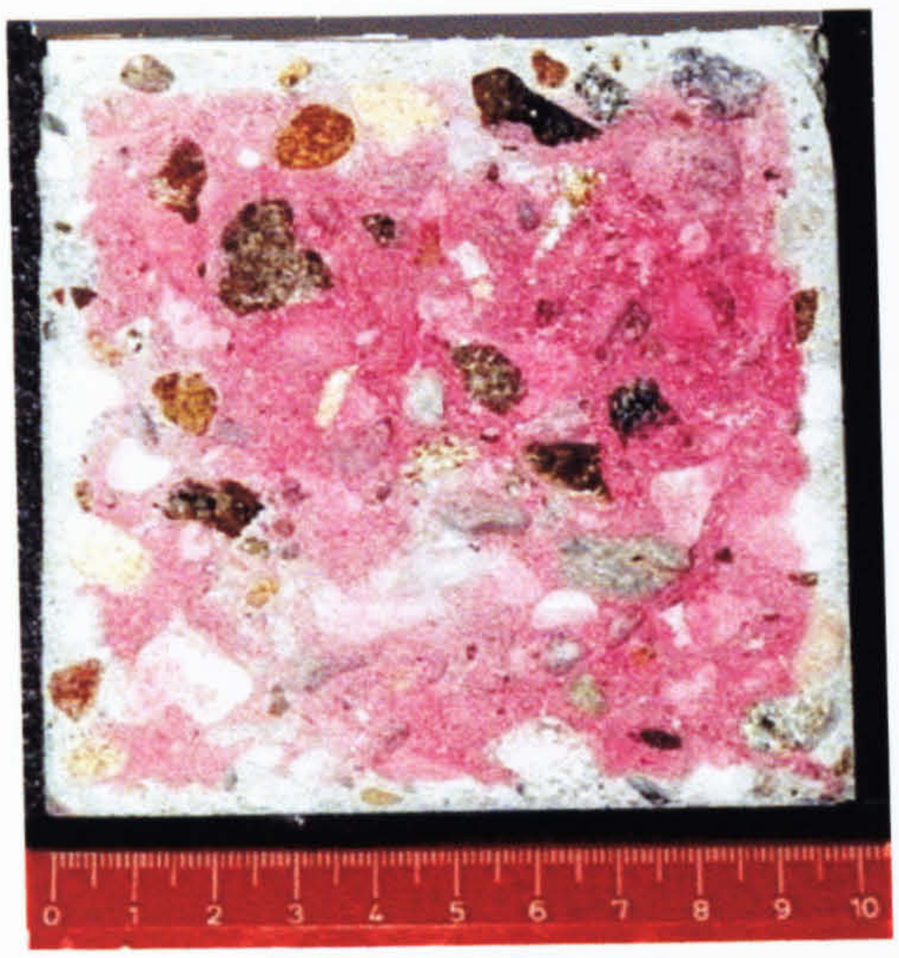
[3] If |N-(cxN)|>0.5 indicates error in calculations

[4] Observed and expected frequencies in extreme intervals are summed so that O≥5 and E≥5.

[5] Yates correction applied for small frequencies such that

$$\chi^2_{corr} = \Sigma \frac{(|O-E|-0.5)^2}{E}$$

*Taken from statistical tables, Kennedy and Neville, 1976



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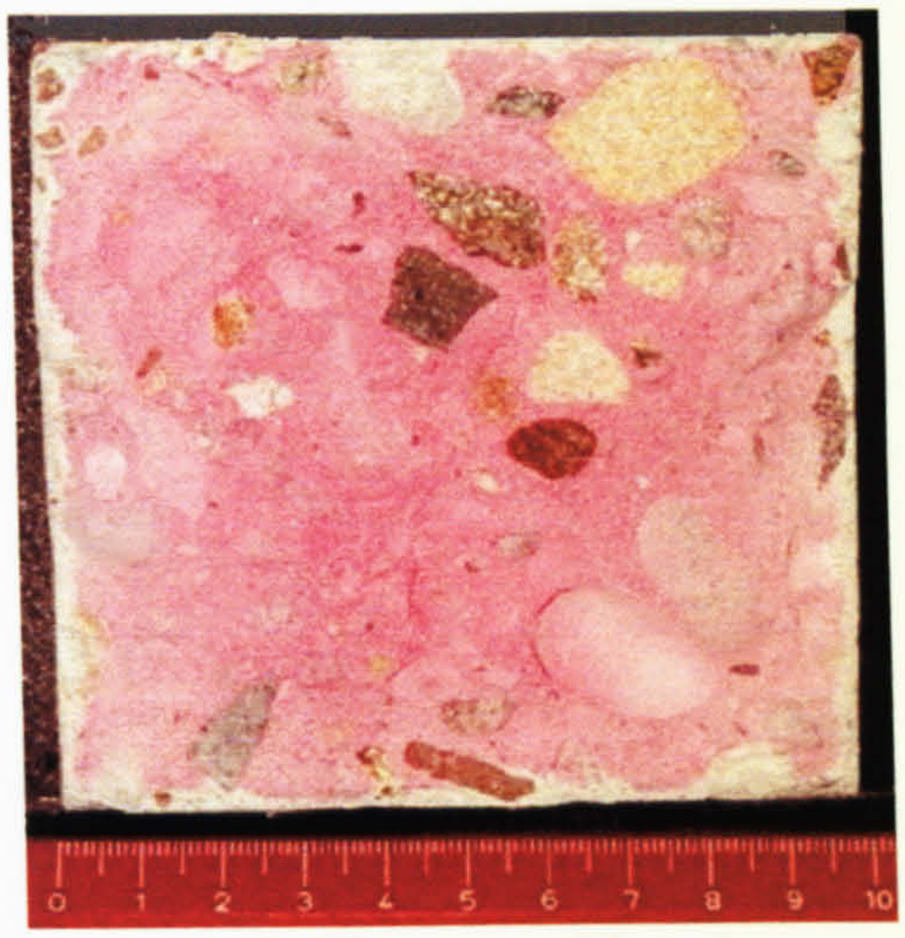

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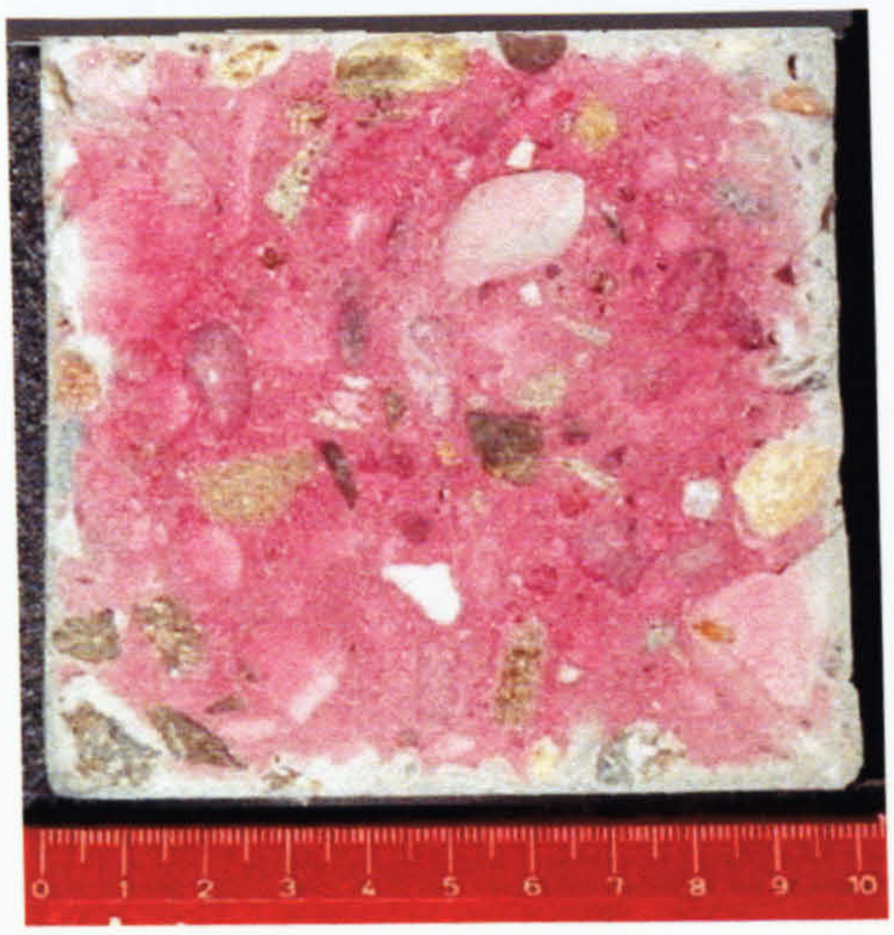

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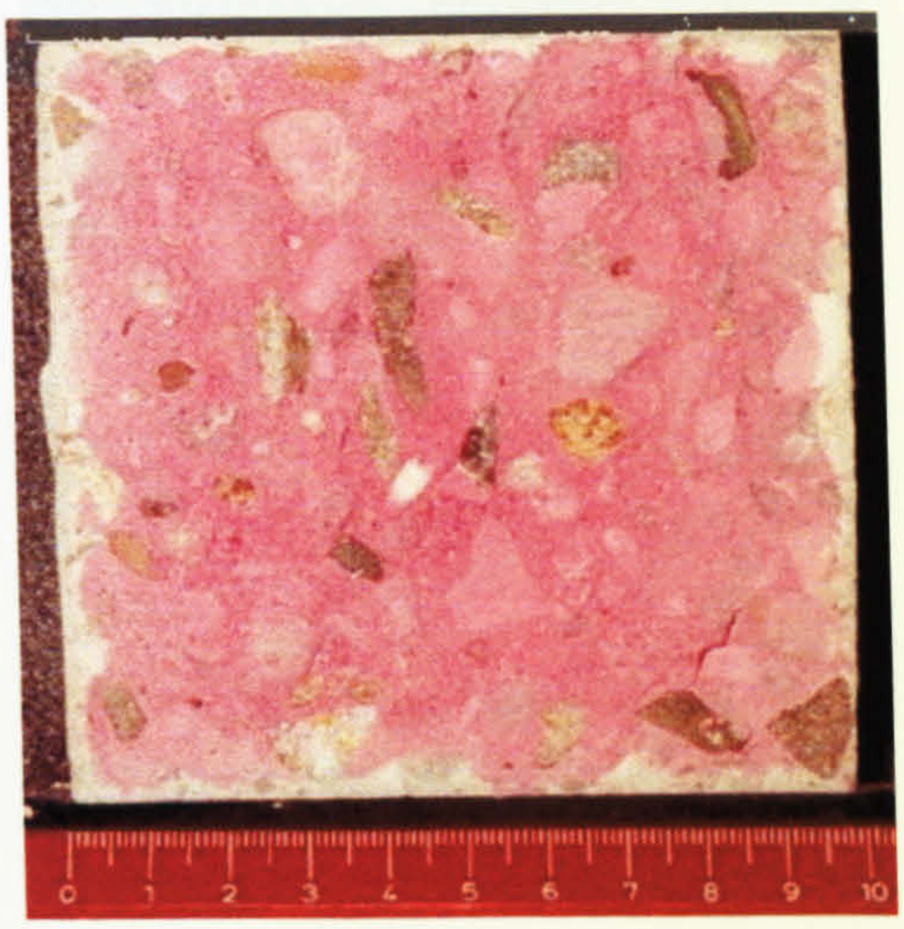
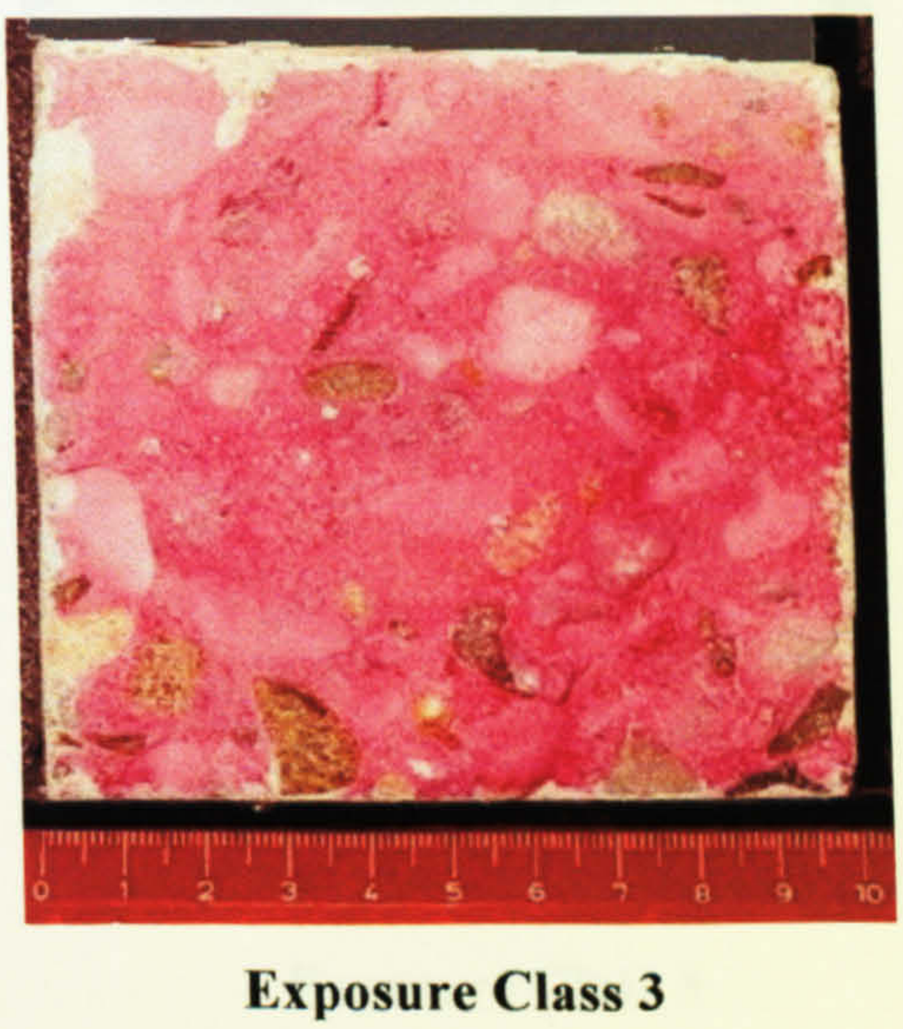


Exposure Class 2

Exposure Class 3

PC/PFA 30% Reference Mix

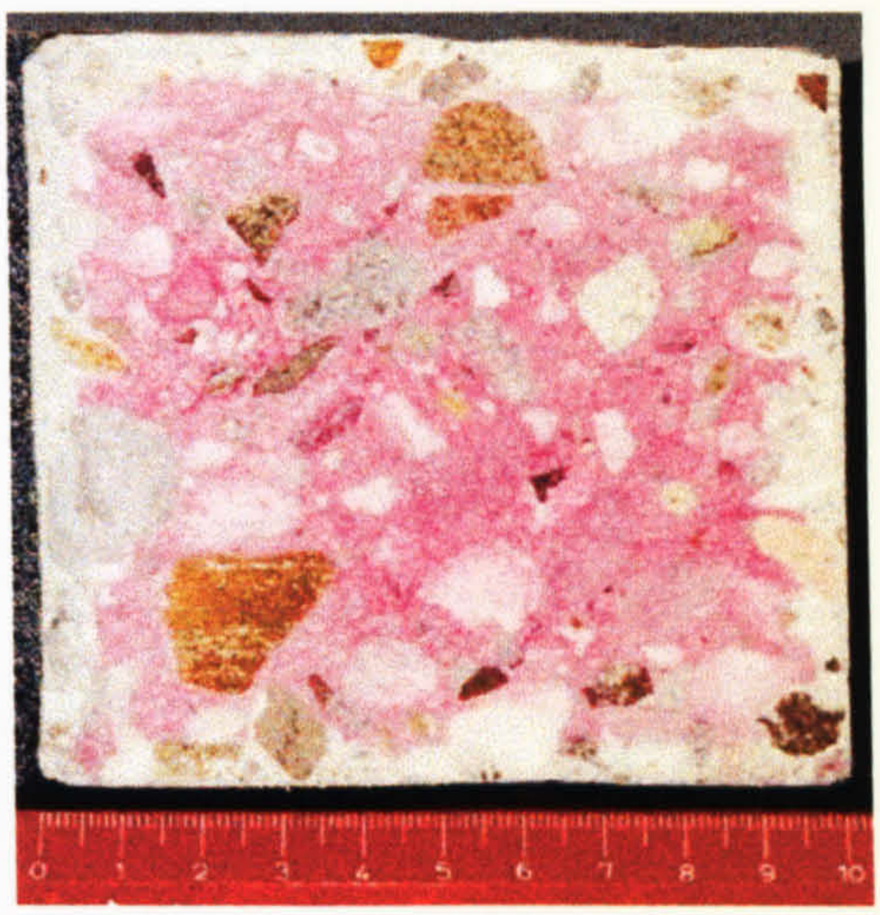


Exposure Class 3

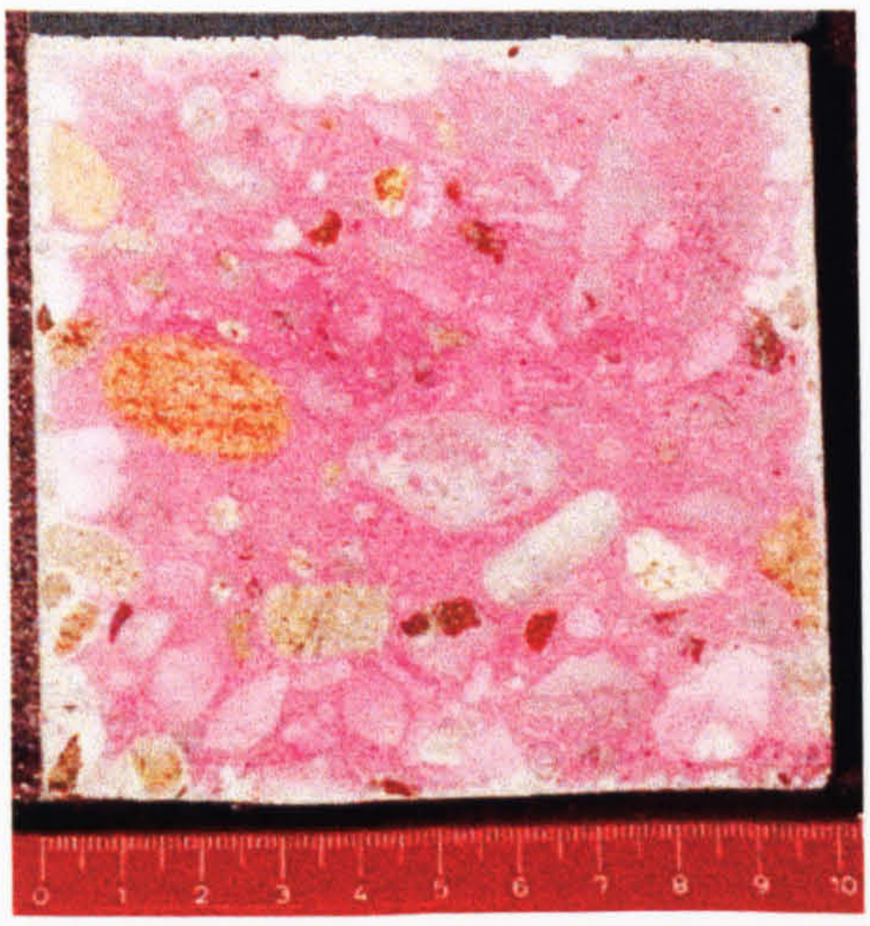
PC

Figure B1 1 year CEN carbonation depths of PC/PFA Reference Mix and PC Mix.

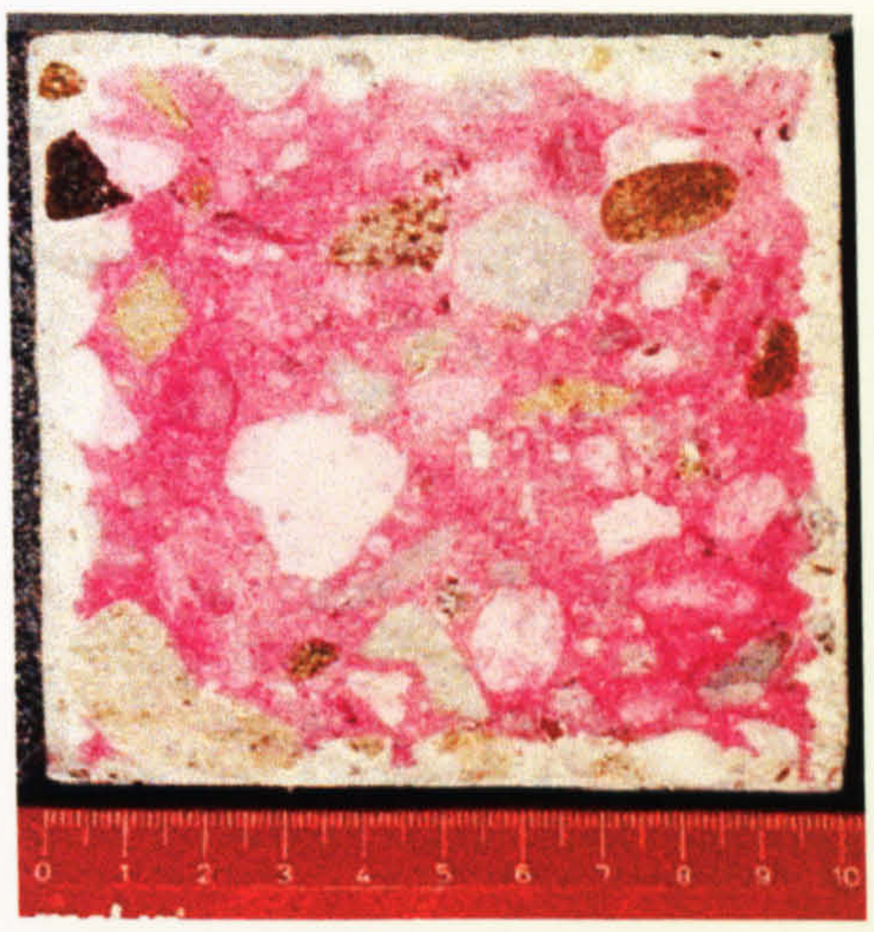
Exposure Class 1



Exposure Class 1



Exposure Class 2



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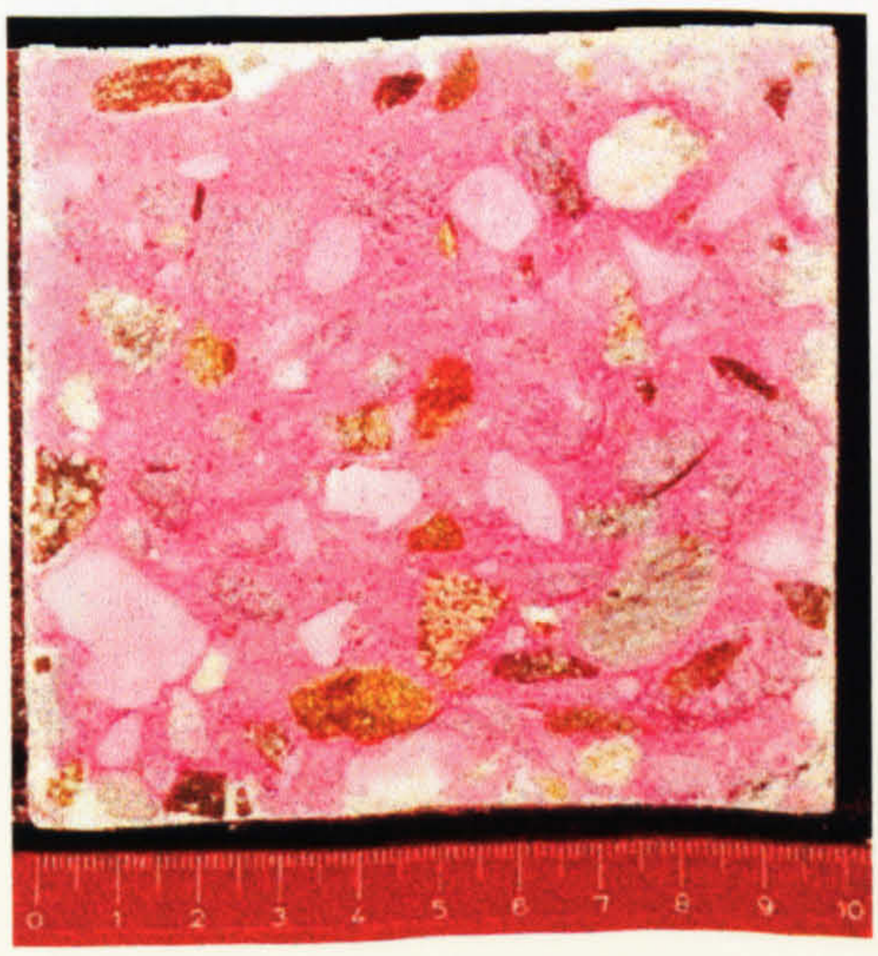


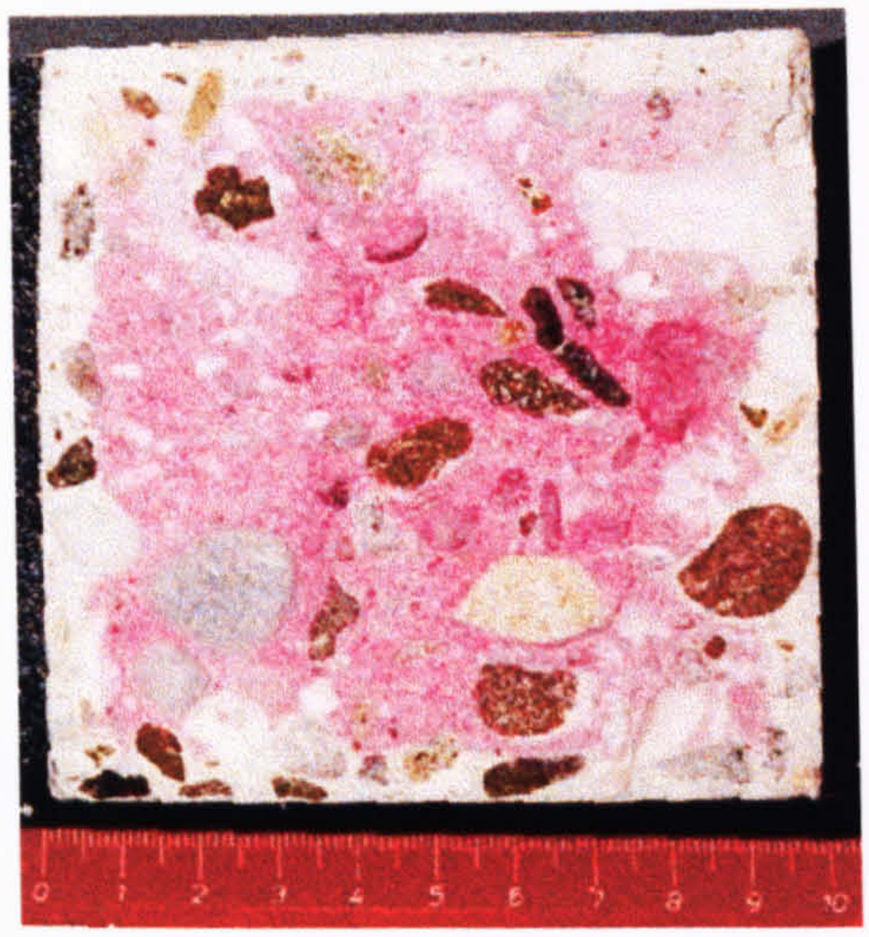
Exposure Class 3

MK 10%

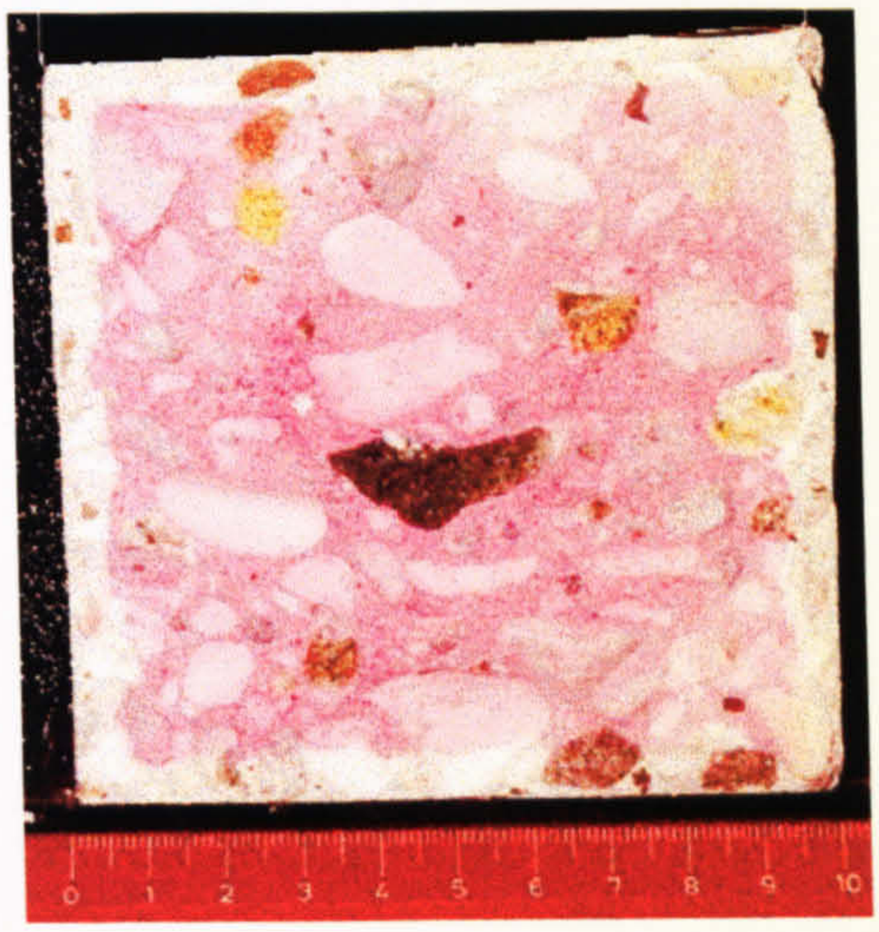
Exposure Class 3

MK 15%

Figure B2 1 year CEN carbonation depths of MK 10% and MK 15% Mixes.

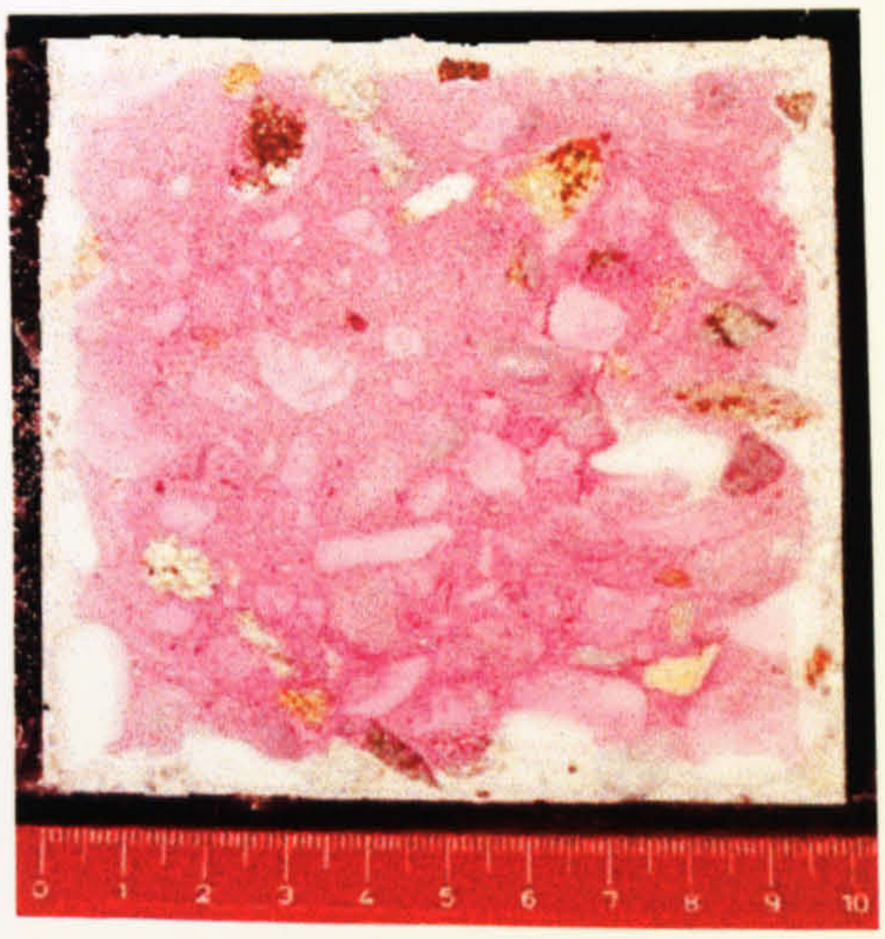


Exposure Class 1

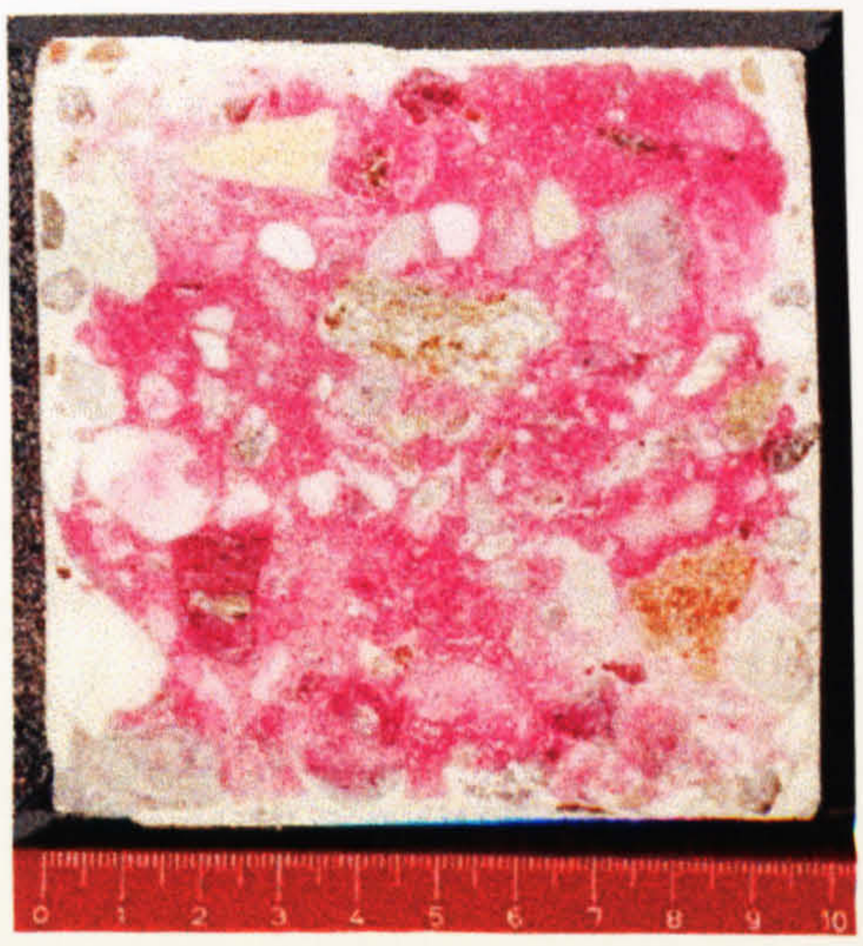


Exposure Class 1

Exposure Class 2

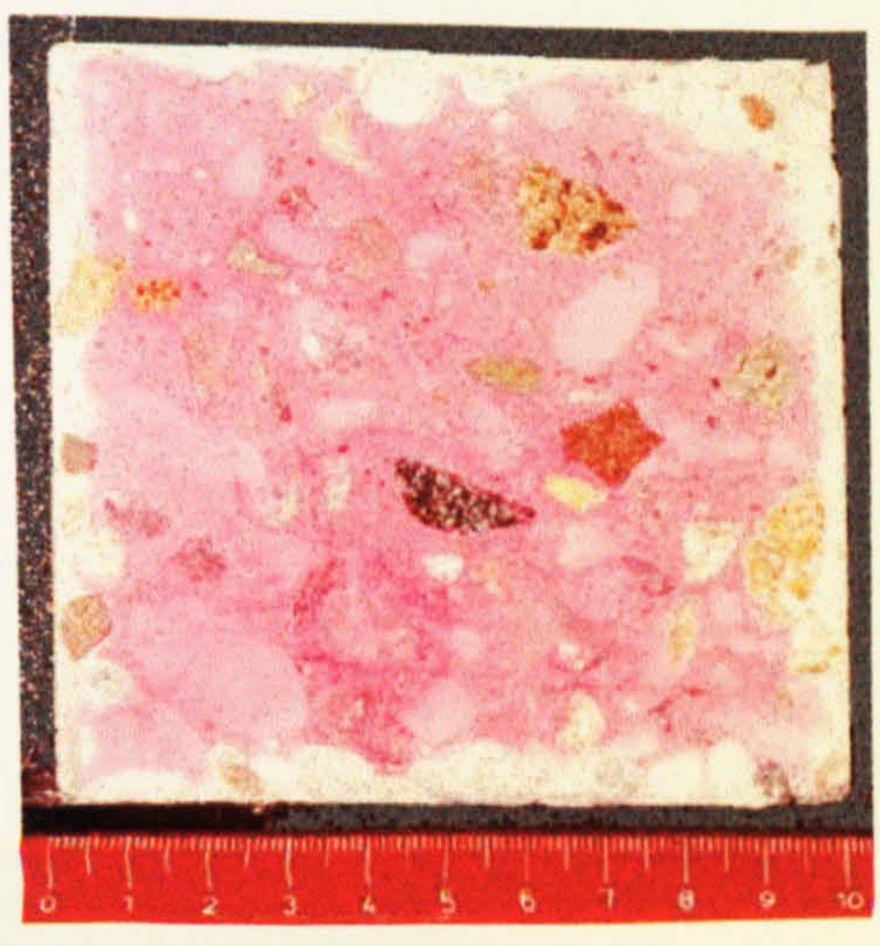


Exposure Class 2



Exposure Class 3

MK 20%



Exposure Class 3

CSF 10%

Figure B3 1 year CEN carbonation depths of MK 20% and CSF 10% Mixes.